



US007471369B2

(12) **United States Patent**
Liang

(10) **Patent No.:** **US 7,471,369 B2**
(45) **Date of Patent:** ***Dec. 30, 2008**

(54) **TRANSMISSIVE OR REFLECTIVE LIQUID CRYSTAL DISPLAY AND PROCESS FOR ITS MANUFACTURE**

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(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 82 days.

This patent is subject to a terminal disclaimer.

6,166,797	A	12/2000	Bruzzzone et al.	
6,172,798	B1	1/2001	Albert et al.	
6,486,932	B1 *	11/2002	Nakao et al.	349/89
6,512,626	B1 *	1/2003	Schmidt	359/296
6,532,052	B1	3/2003	Khan et al.	
6,697,129	B1	2/2004	Nishi et al.	
6,751,007	B2	6/2004	Liang et al.	
6,812,977	B1 *	11/2004	Iwamatsu et al.	349/73
6,865,012	B2	3/2005	Liang et al.	
6,930,818	B1 *	8/2005	Liang et al.	359/296
6,987,605	B2	1/2006	Liang et al.	

(21) Appl. No.: **10/960,232**

(22) Filed: **Oct. 6, 2004**

(65) **Prior Publication Data**

US 2005/0099575 A1 May 12, 2005

Related U.S. Application Data

(63) Continuation-in-part of application No. 10/794,318, filed on Mar. 5, 2004, now Pat. No. 7,095,477, which is a continuation-in-part of application No. 09/759,212, filed on Jan. 11, 2001, now Pat. No. 6,795,138.

(51) **Int. Cl.**
G02F 1/1339 (2006.01)

(52) **U.S. Cl.** **349/156**; 349/89

(58) **Field of Classification Search** None
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

3,680,950	A	8/1972	Haas et al.
3,704,056	A	11/1972	Wysocki et al.
4,097,127	A	6/1978	Haas et al.
5,268,782	A	12/1993	Wenz et al.
5,384,067	A	1/1995	Doane et al.
5,453,863	A	9/1995	West et al.

FOREIGN PATENT DOCUMENTS

JP	6242423	9/1994
----	---------	--------

(Continued)

OTHER PUBLICATIONS

U.S. Appl. No. 10/771,848, filed Feb. 2004, Liang et al.

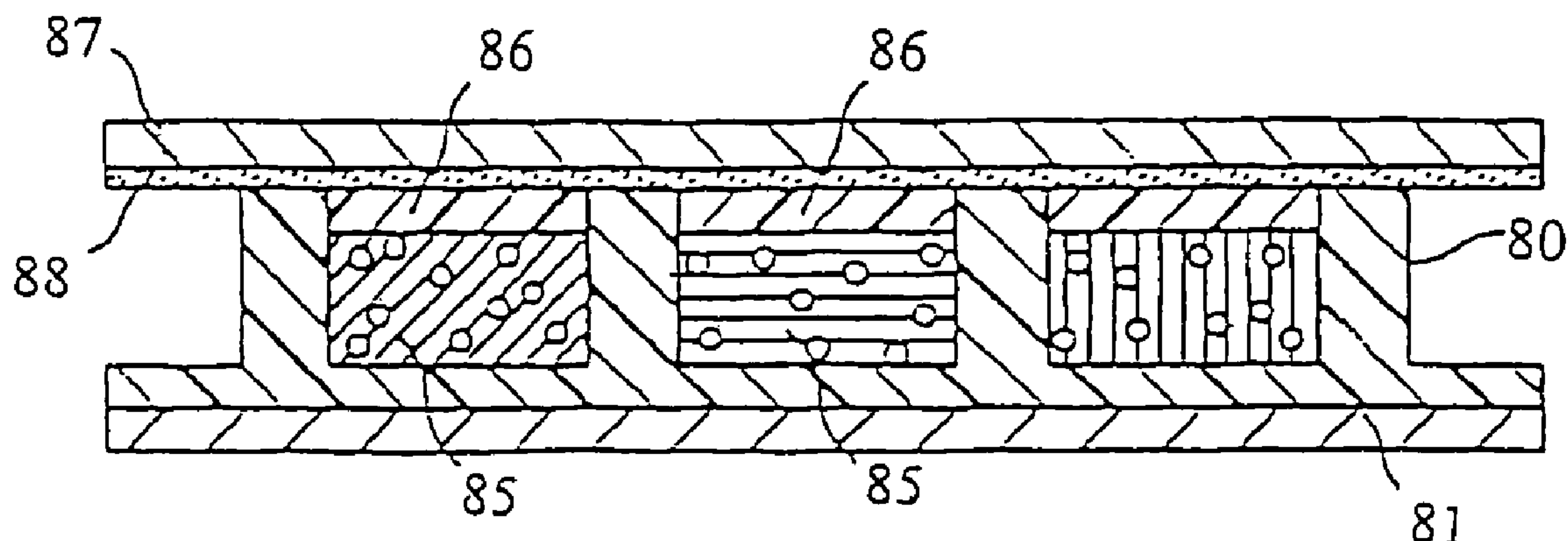
(Continued)

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(57) **ABSTRACT**

This invention relates to cholesteric liquid crystal (LC) displays comprising cells of well-defined shape, size and aspect ratio which cells are filled with a liquid crystal composition preferably containing dichroic dye(s), and novel processes for their manufacture.

37 Claims, 18 Drawing Sheets



FOREIGN PATENT DOCUMENTS

JP	11-271780	10/1999
JP	2000 310784	11/2000

OTHER PUBLICATIONS

Allen, K. (Oct. 2003). Electrophoretics Fulfilled. *Emerging Displays Review: Emerging Display Technologies, Monthly Report*—Oct. 2003, 9-14.

Chaug, Y.S., Haubrich, J.E., Sereda, M. and Liang, R.C. (Apr. 2004). Roll-to-Roll Processes for the Manufacturing of Patterned Conductive Electrodes on Flexible Substrates. *Mat. Res. Soc. Symp. Proc.*, vol. 814, I9.6.1.

Chen, S.M. (Jul. 2003) The Applications for the Revolutionary Electronic Paper Technology. *OPTO News & Letters*, 102, 37-41. (in Chinese, English abstract attached, full translation available upon request).

Chen, S.M. (May 2003) The New Applications and the Dynamics of Companies. *TRI*, 1-10. (In Chinese, English abstract attached, full translation available upon request).

Chung, J., Hou, J., Wang, W., Chu, L.Y., Yao, W., & Liang, R.C. (Dec. 2003). Microcup(R) Electrophoretic Displays, Grayscale and Color Rendition. *IDW*, AMD2/EP1-2, 243-246.

Ciferri, A. et al, "Polymer Liquid Crystals", Academic Press, Inc. (1982).

Ho, C., & Liang, R.C. (Dec. 2003). *Microcup (R) Electronic Paper by Roll-to-Roll Manufacturing Processes*. Presentation conducted at FEG, Nei-Li, Taiwan.

Hou, J., Chen, Y., Li, Y., Weng, X., Li, H. And Pereira, C. (May 2004). Reliability and Performance of Flexible Electrophoretic Displays by Roll-to-Roll Manufacturing Processes. *SID Digest*, 32.3, 1066-1069.

Kuschel, K. et al, "Chiral Dopants for LCD Applications", *SID Digest*, LP-4/F. Kuschel, pp. 554-557 (2002).

Lee, H., & Liang, R.C. (Jun. 2003) SiPix Microcup(R) Electronic Paper—An Introduction. *Advanced Display*, 3, 4-9 (in Chinese, English abstract attached, full translation available upon request).

Liang, R.C., Hou, J., Chung, J., Wang, X., Pereira, C., & Chen, Y. (2003). Microcup(R) Active and Passive Matrix Electrophoretic Displays by A Roll-to-Roll Manufacturing Processes. *SID Digest*, 20.1.

Liang, R.C., Hou, J., Zang, H.M., Chung, J., & Tseng, S. (2003). Microcup(R) displays : Electronic Paper by Roll-to-Roll Manufacturing Processes. *Journal of the SID*, 11(4), 621-628.

Liang, R.C., Hou, J., Zang, H.M., & Chung, J. (Feb. 2003). *Passive Matrix Microcup(R) Electrophoretic Displays*. Paper presented at the IDMC, Taipei, Taiwan.

Liang, R.C., Hou, J., & Zang, H.M. (Dec. 2002) Microcup Electrophoretic Displays by Roll-to-Roll Manufacturing Processes. *IDW*, EP2-2, 1337-1340.

Liang, R.C. (Feb. 2003) *Microcup(R) Electrophoretic and Liquid Crystal Displays by Roll-to-Roll Manufacturing Processes*. Presentation conducted at the Flexible Microelectronics & Displays Conference of U.S. Display Consortium, Phoenix, Arizona, USA.

Liang, R.C. (Apr. 2004). *Microcup Electronic Paper by Roll-to-Roll Manufacturing Process*. Presentation at the Flexible Displays & Electronics 2004 of Intertech, San Fransisco, California, USA.

Liang, R.C., Zang, H.M., Wang, X., Chung, J. & Lee, H., (Jun./Jul. 2004) << Format Flexible Microcup (R) Electronic Paper by Roll-to-Roll Manufacturing Process >>, Presentation conducted at the 14th FPD Manufacturing Technology EXPO & Conference.

March, N., et al "Polymers, Liquid Crystals, and Low Dimensional Solids", Plenum Press (1984).

Nikkei Microdevices. (Dec. 2002) Newly-Developed Color Electronic Paper Promises—Unbeatable Production Efficiency. *Nikkei Microdevices*, 3. (in Japanese, with English translation).

Stephenson, S.W. et al, "Development of a Flexible Electronic Display Using Photographic Technology", *SID Digest*, pp. 774-777 (2004).

Wang, X., Kiluk, S., Chang, C., Wu, Y., & Liang, R.C. (Feb. 2004). Microcup (R) Electronic Paper and the Converting Processes. *ASID*, 10.1.2-26, 396-399 Nanjing, China.

Wu, S.T. et al, "Reflective Liquid Crystal Displays", John Wiley & Sons Ltd. (2001).

Yang, D.K. et al, "Bistable Polymer Dispersed Cholesteric Reflective Display", *SID Digest*, pp. 959-961 (2003).

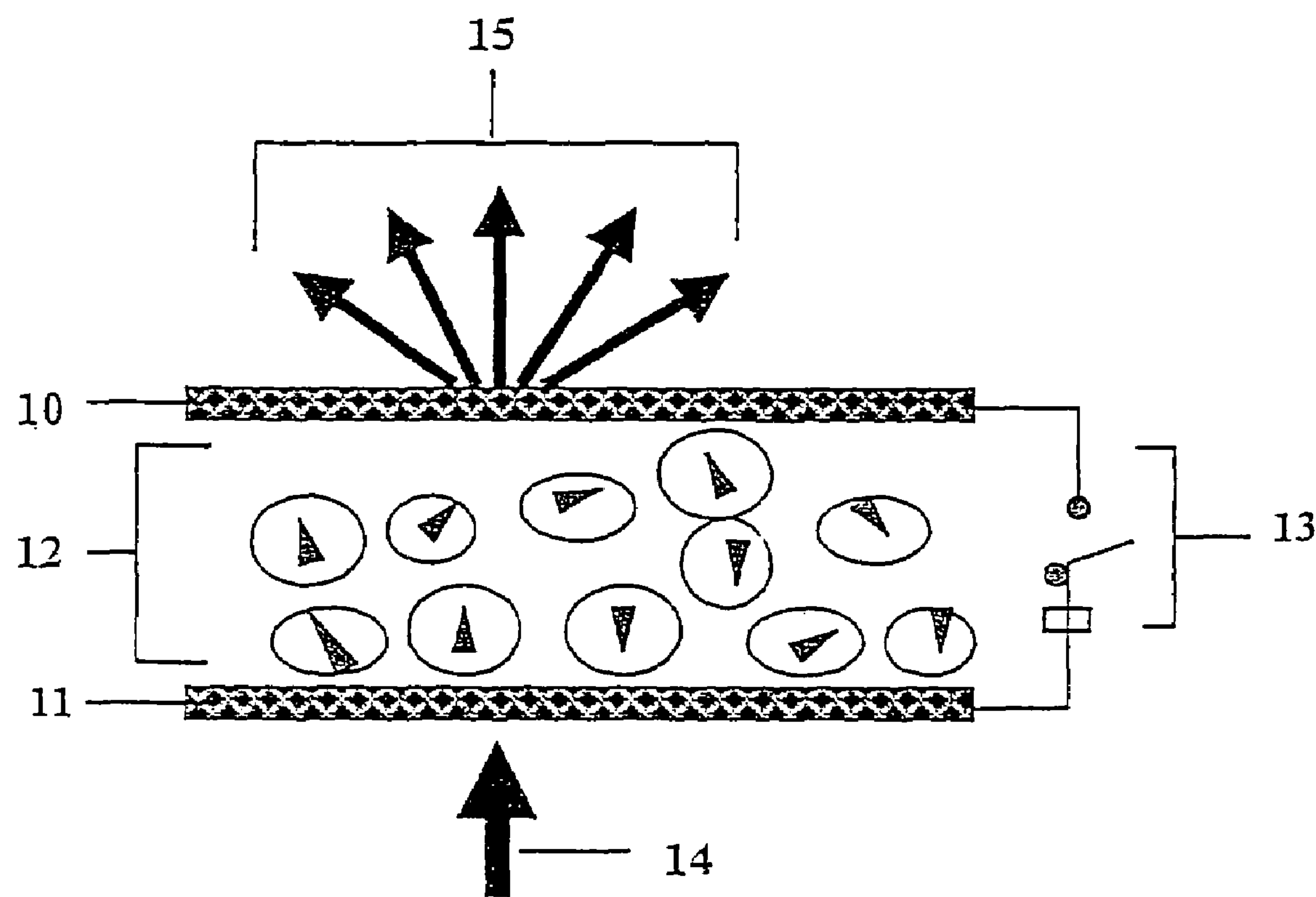
Zang, H.M., Hwang, J.J., Gu, H., Hou, J., Weng, X., Chen, Y., et al. (Jan. 2004). Threshold and Grayscale Stability of Microcup (R) Electronic Paper. *Proceeding of SPIE-IS&T Electronic Imaging*, *SPIE* vol. 5289, 102-108.

Zang, H.M., & Liang, R.C. (2003) Microcup Electronic Paper by Roll-to-Roll Manufacturing Processes. *The Spectrum*, 16(2), 16-21.

Zang, H.M. (Oct. 2003). *Microcup (R) Electronic Paper by Roll-to-Roll Manufacturing Processes*. Presentation conducted at the Advisory Board Meeting, Bowling Green State University, Ohio, USA.

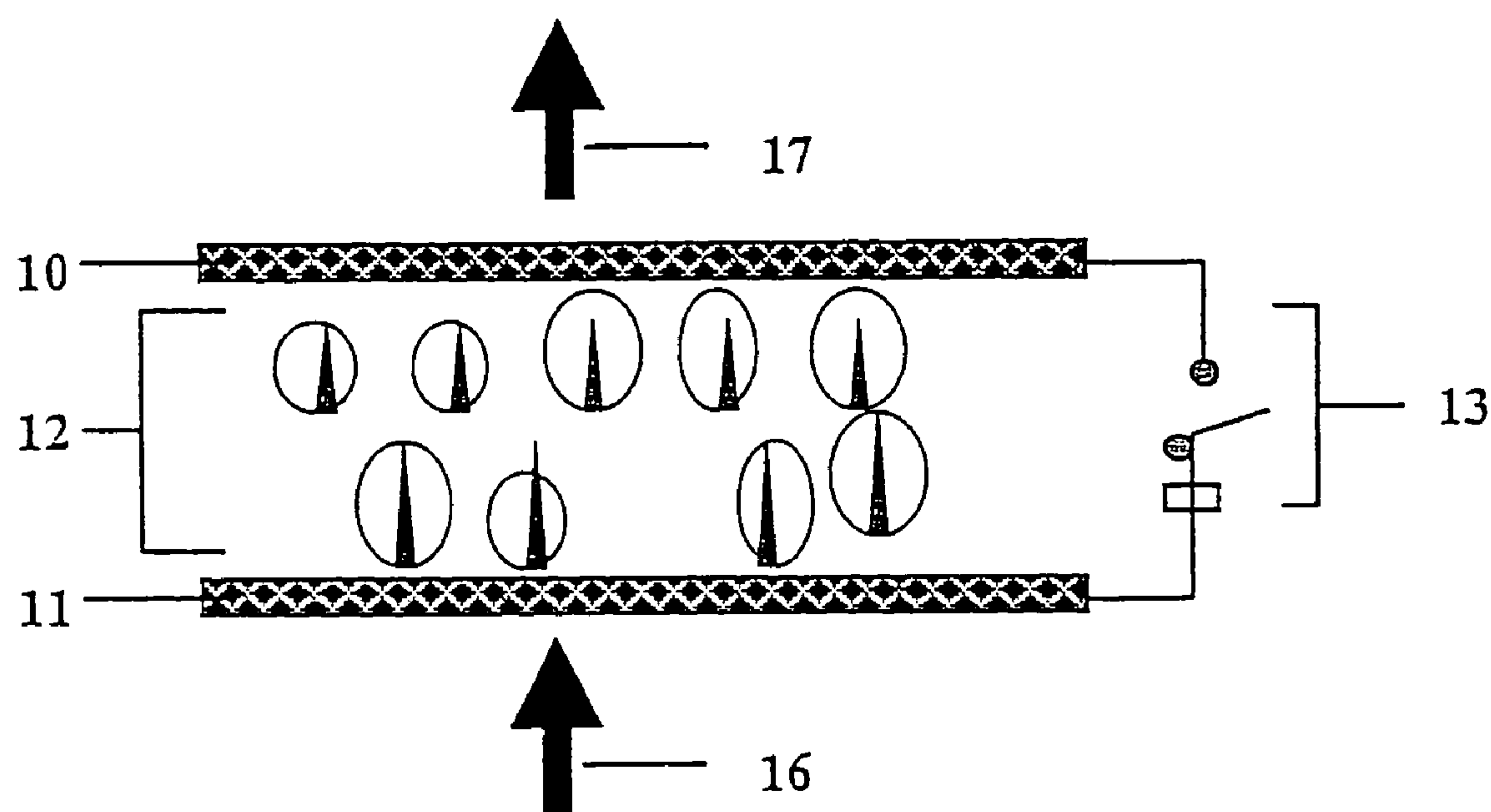
Zang, H.M. (Feb. 2004). *Microcup Electronic Paper*. Presentation conducted at the Displays & Microelectronics Conference of U.S. Display Consortium, Phoenix, Arizona, USA.

* cited by examiner



Off State
Scatters Light, White

FIG. 1a



On State
Transparent, Clear

FIG. 1b

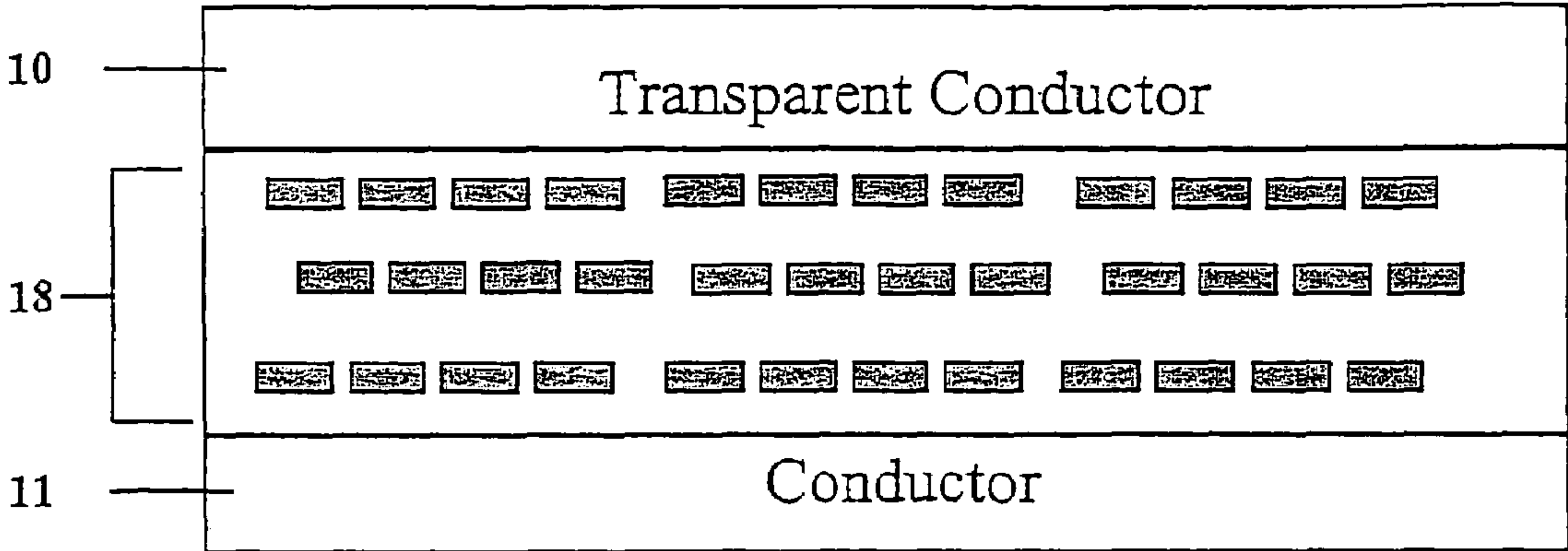


FIG. 1c

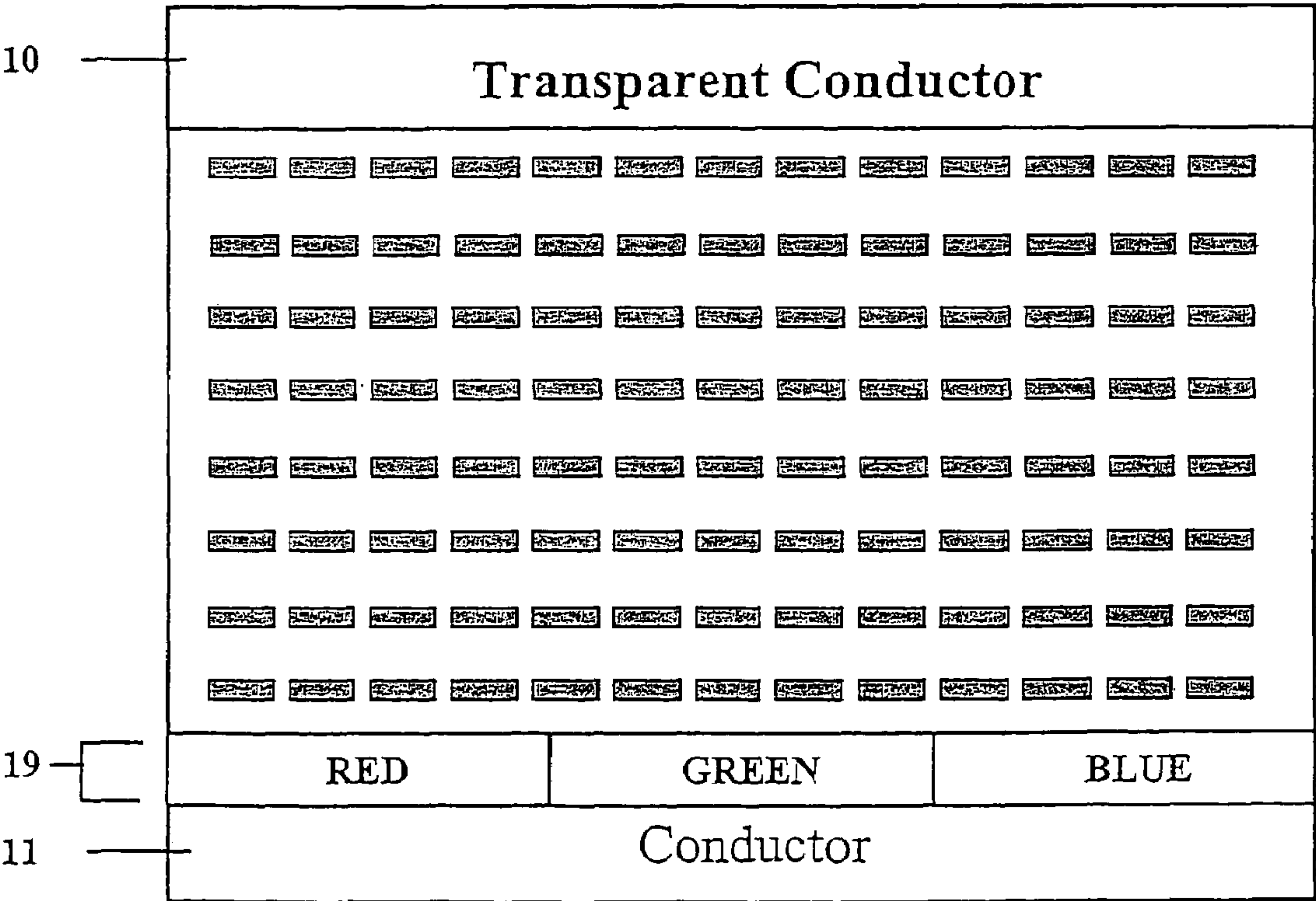


FIG. 1d

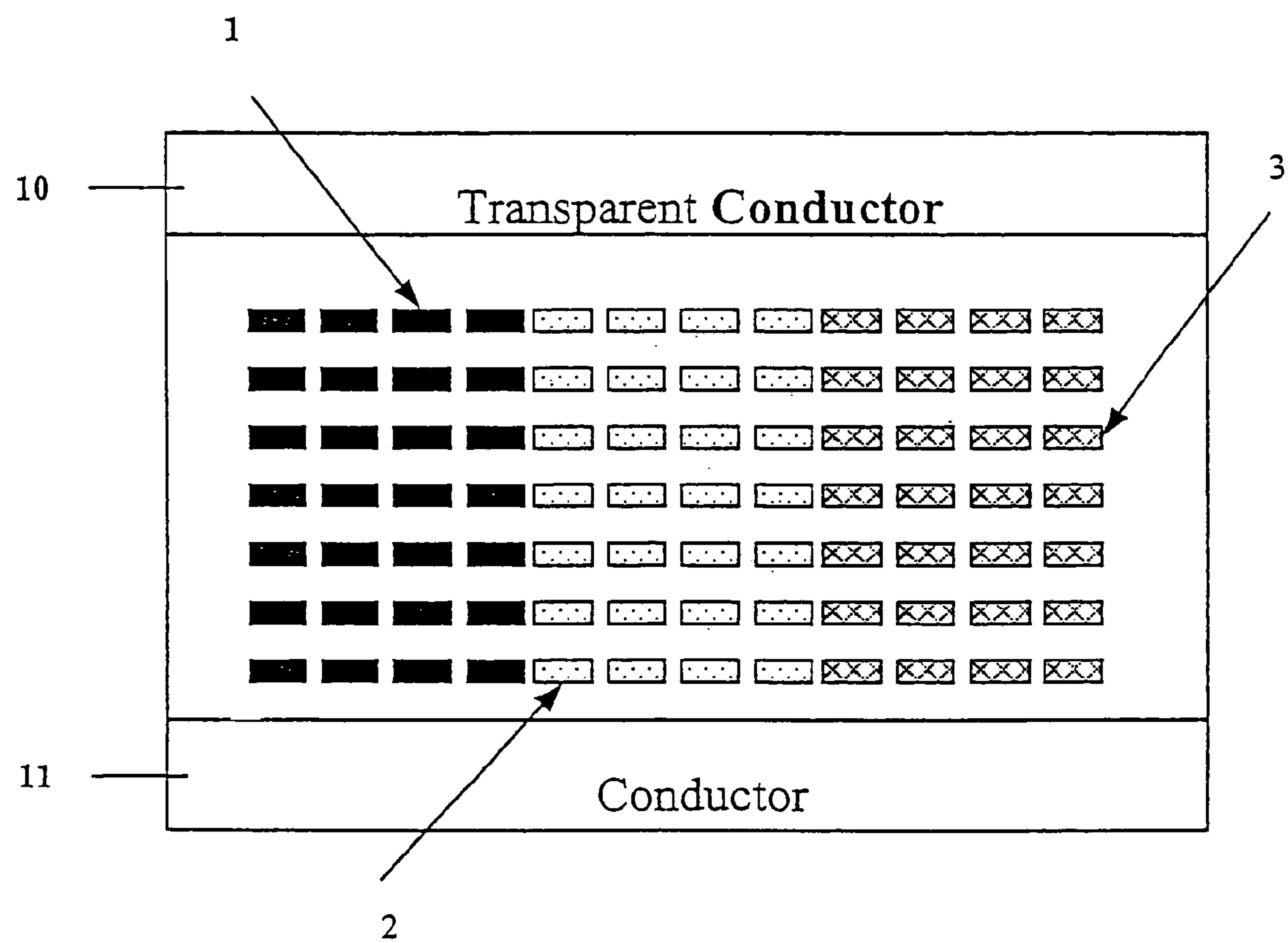


FIG. 1e

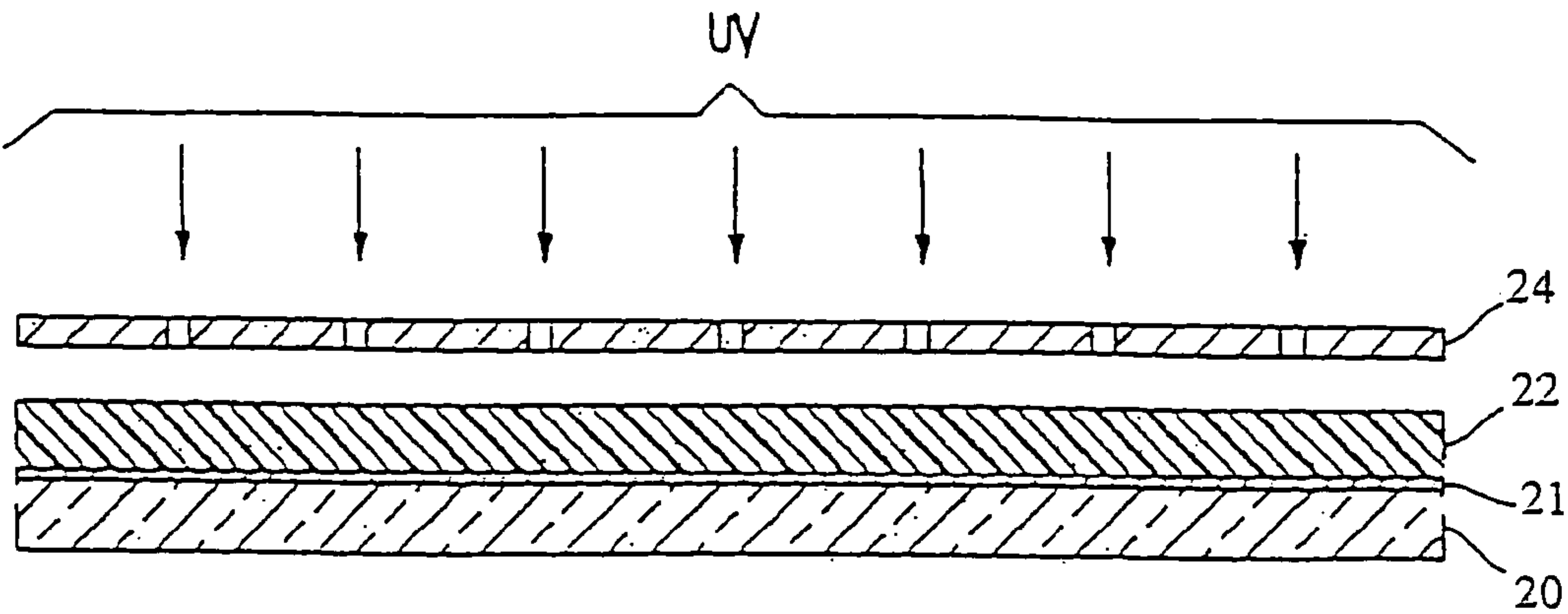


FIG. 2a

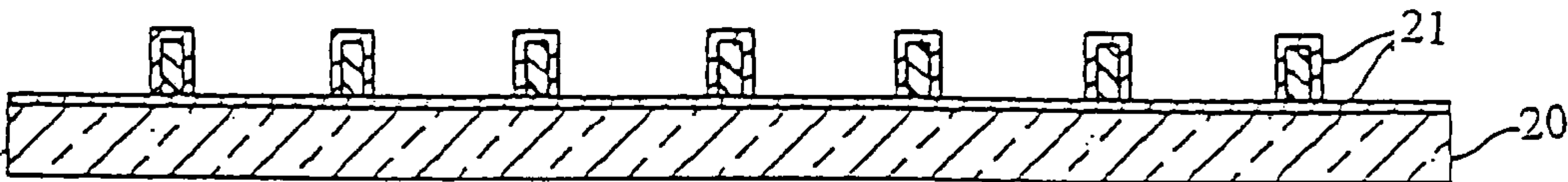


FIG. 2b

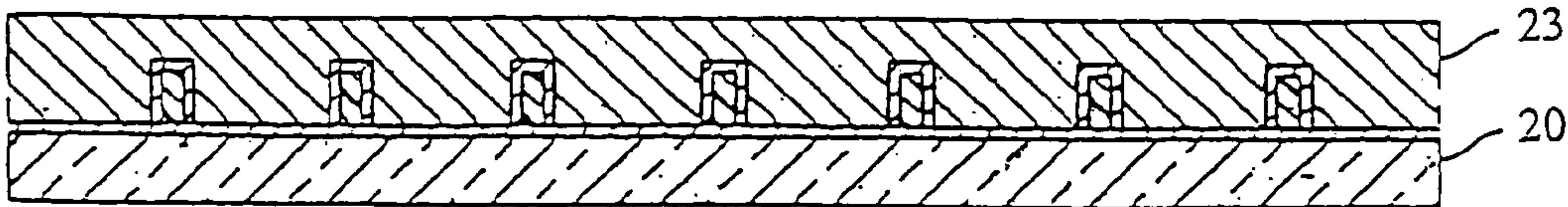


FIG. 2c



FIG. 2d

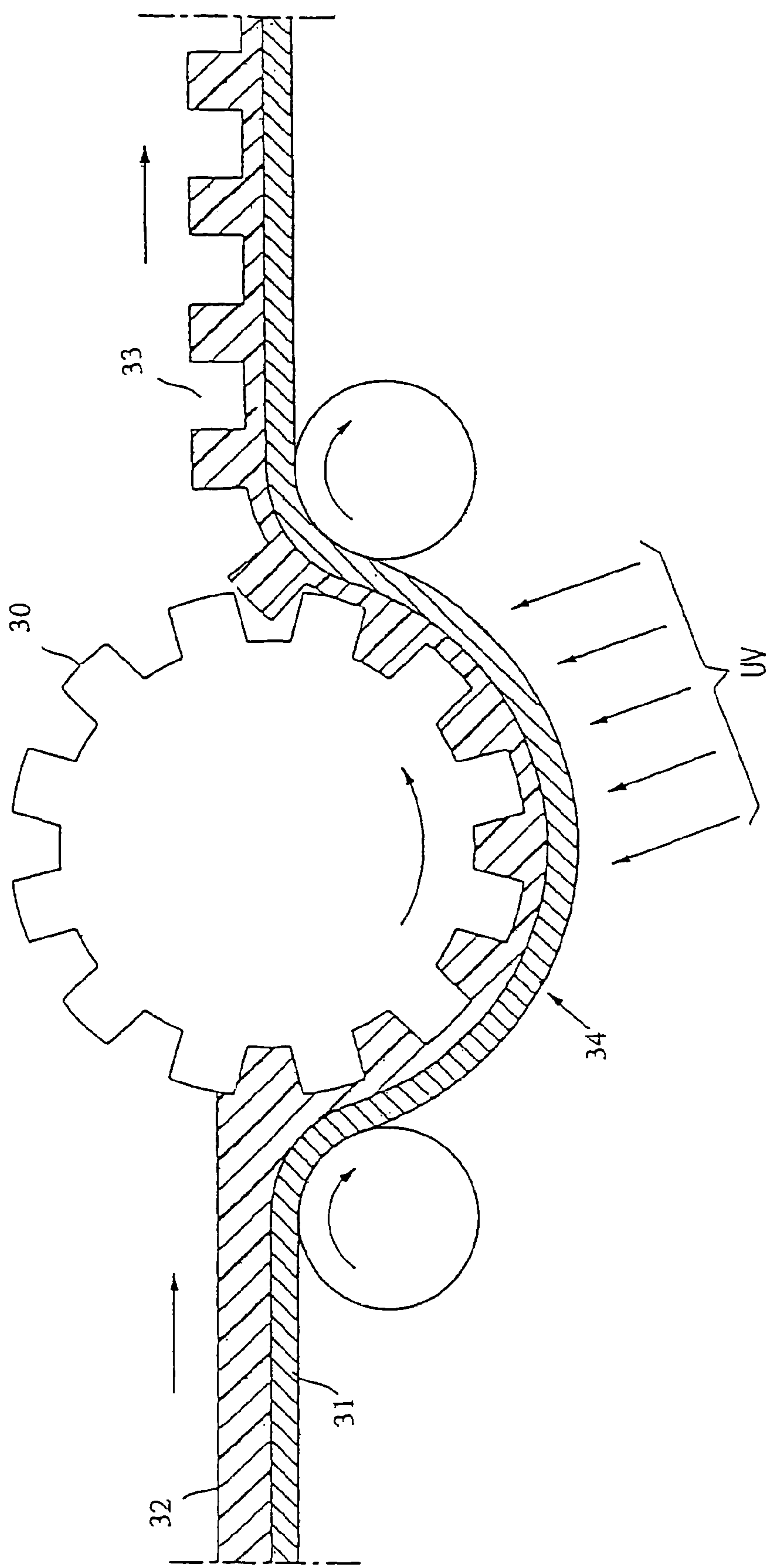


FIG. 3a

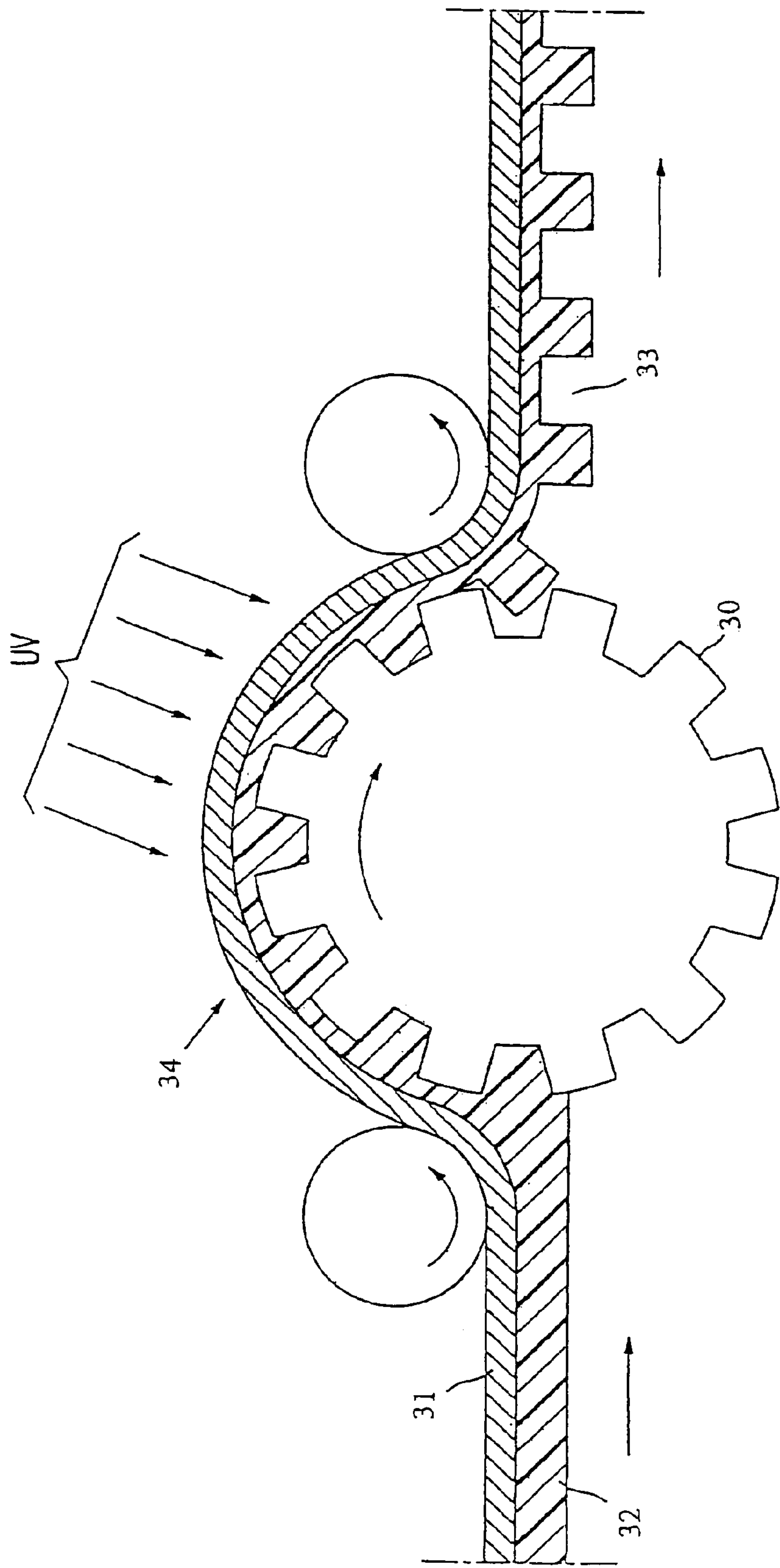


FIG. 3b

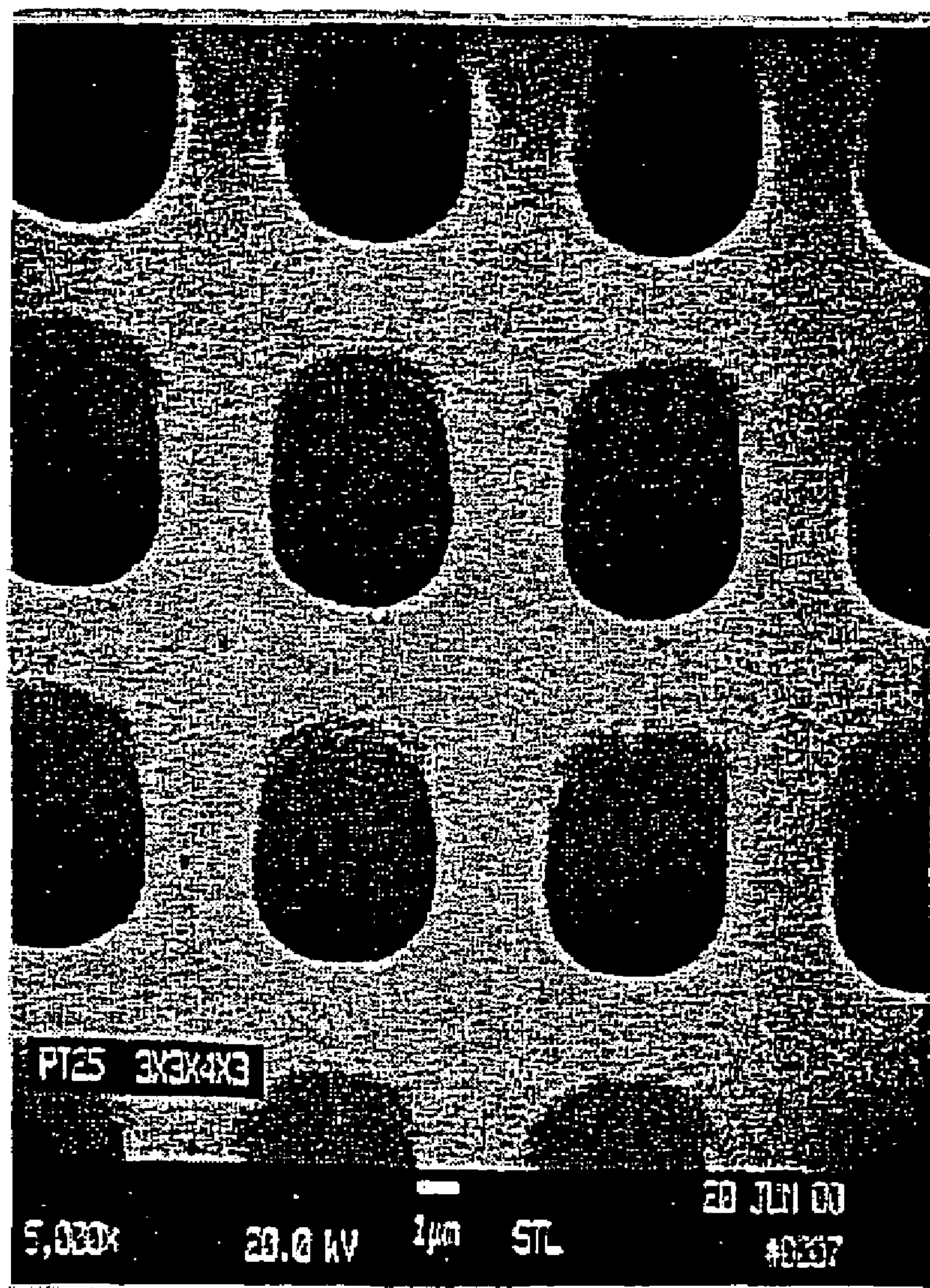


FIG. 4a

SEM Micrograph of Microcups
4.3 x 4.3 x 4.4 x 2.4 μm (5000x)
(L x W x D x Wall)
Opening Area 41%

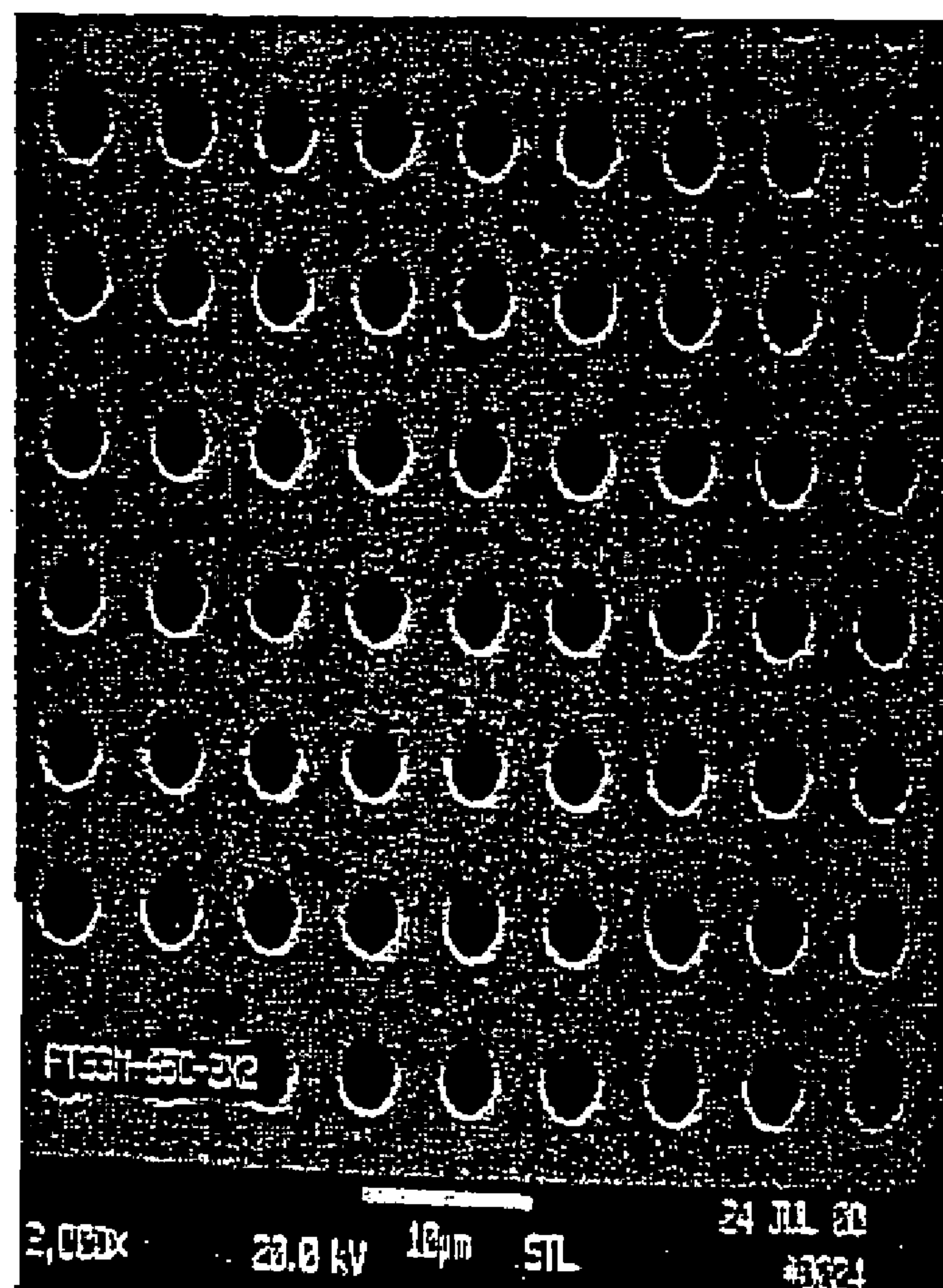


FIG. 4b

SEM Micrograph of Microcups
3.5 x 3.5 x 3.5 x 2.5 μm (2000x)
(L x W x D x Wall)
Opening Area 34%

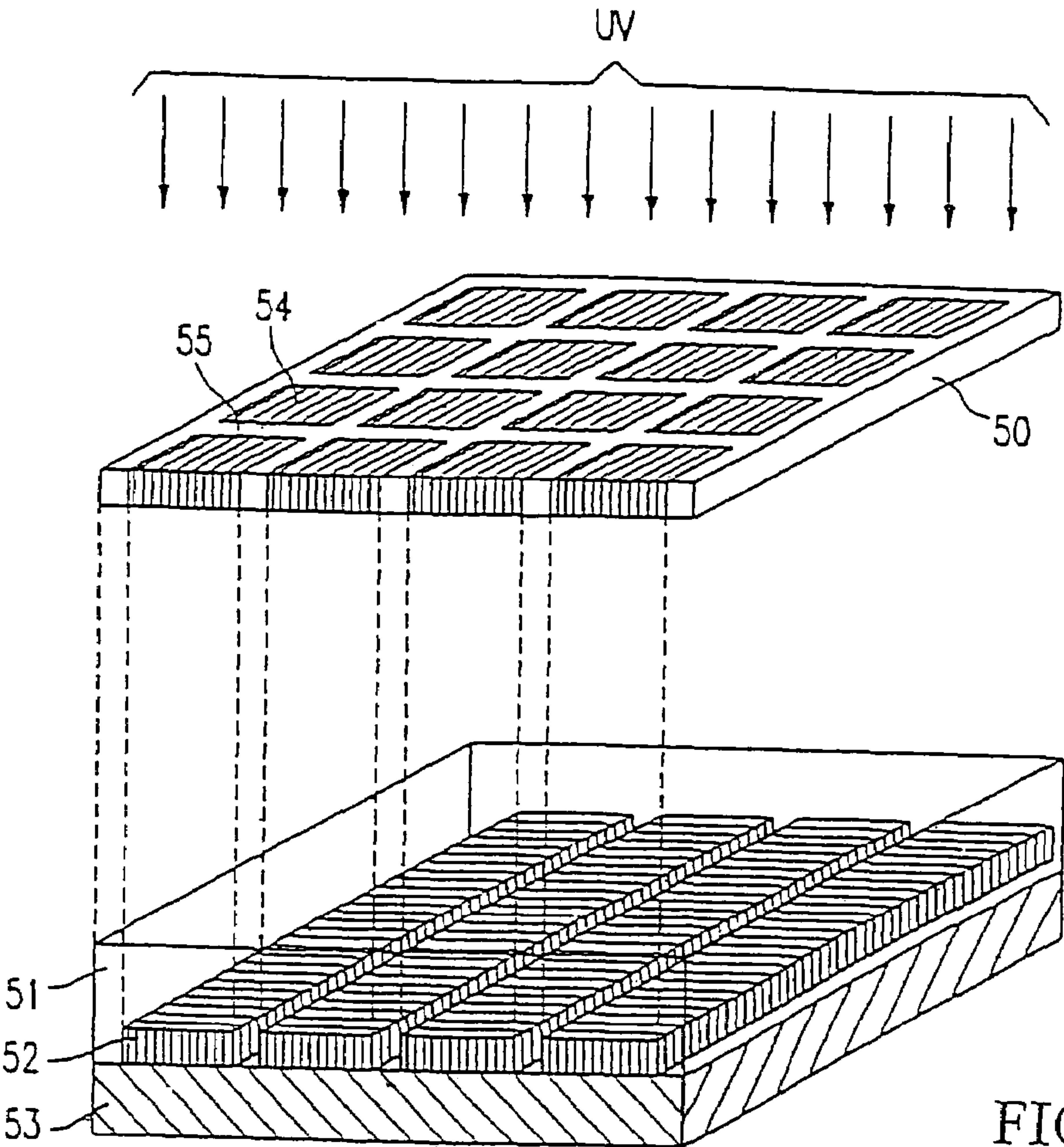


FIG. 5a1

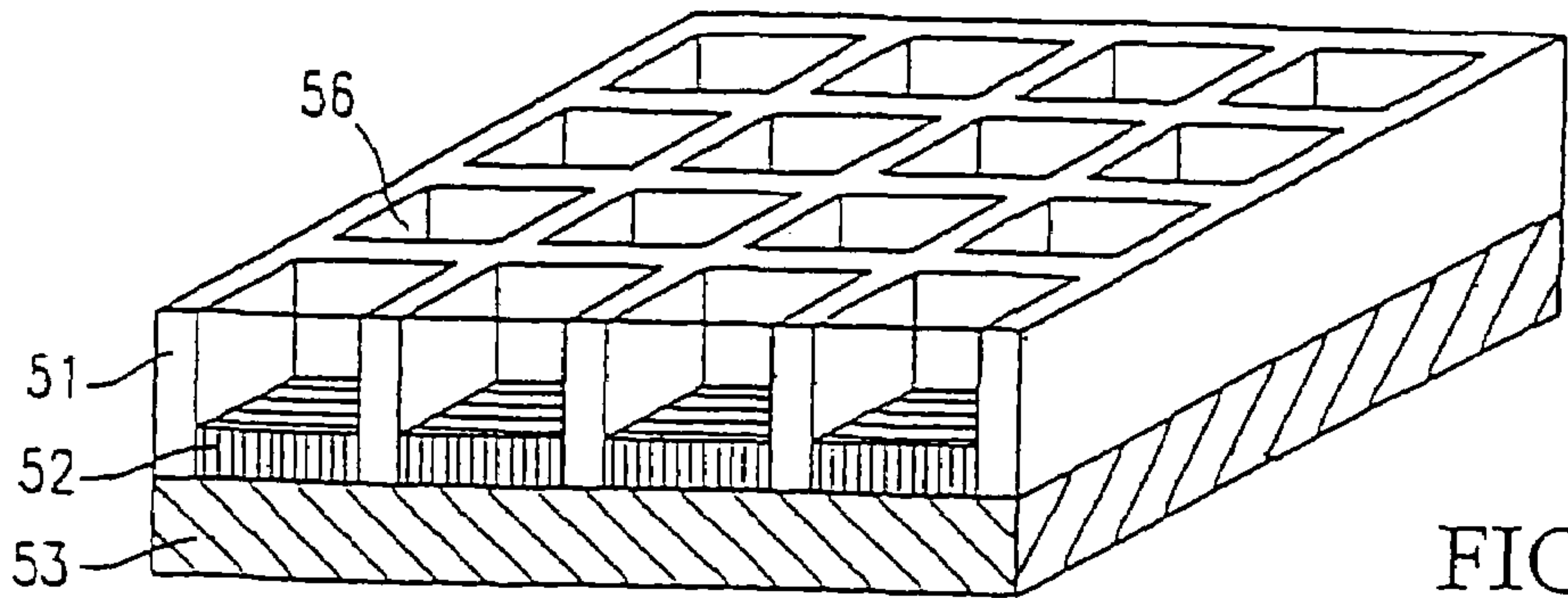


FIG. 5a2

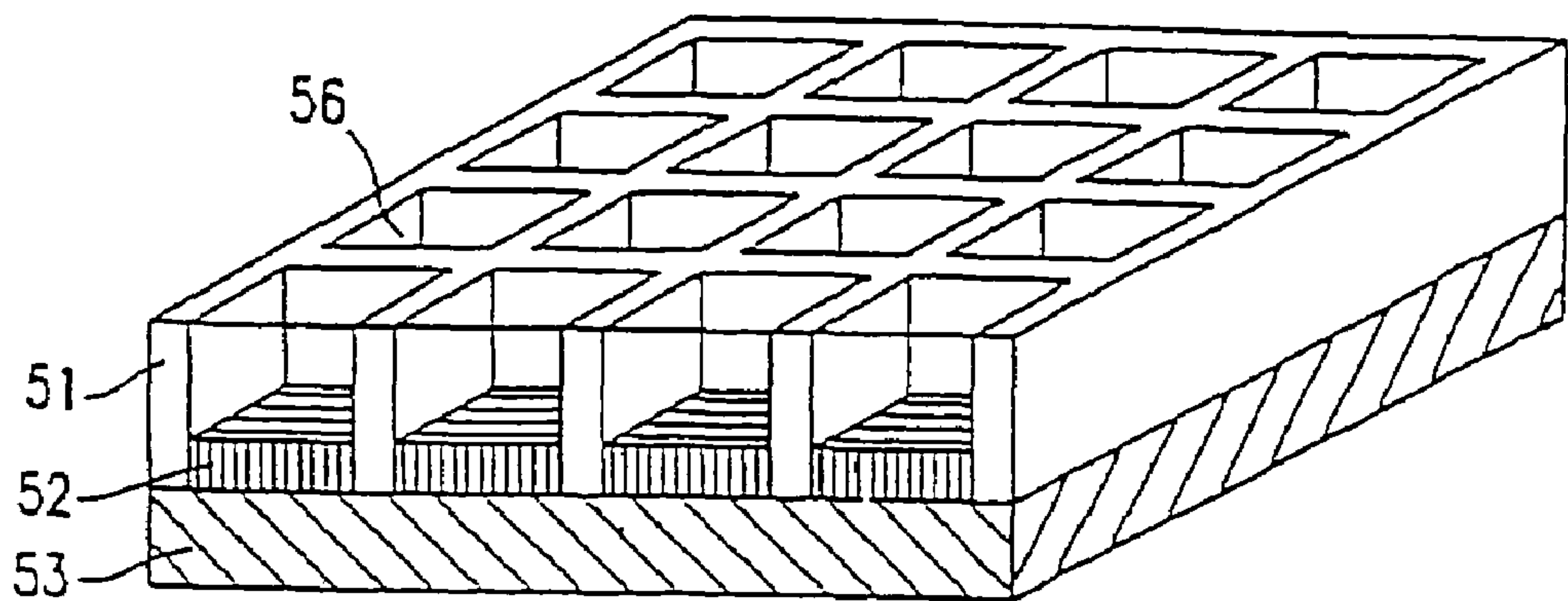


FIG. 5b2

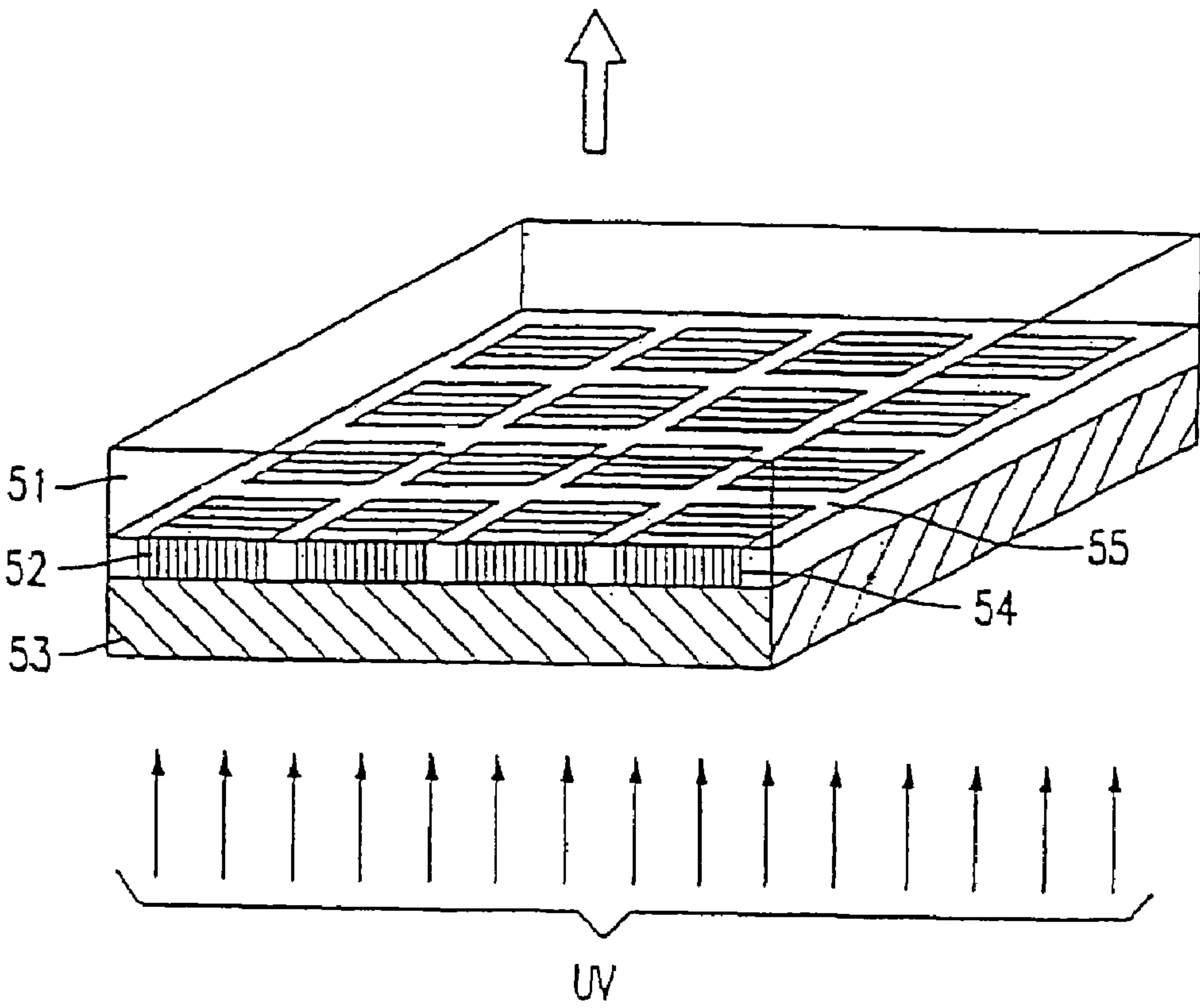
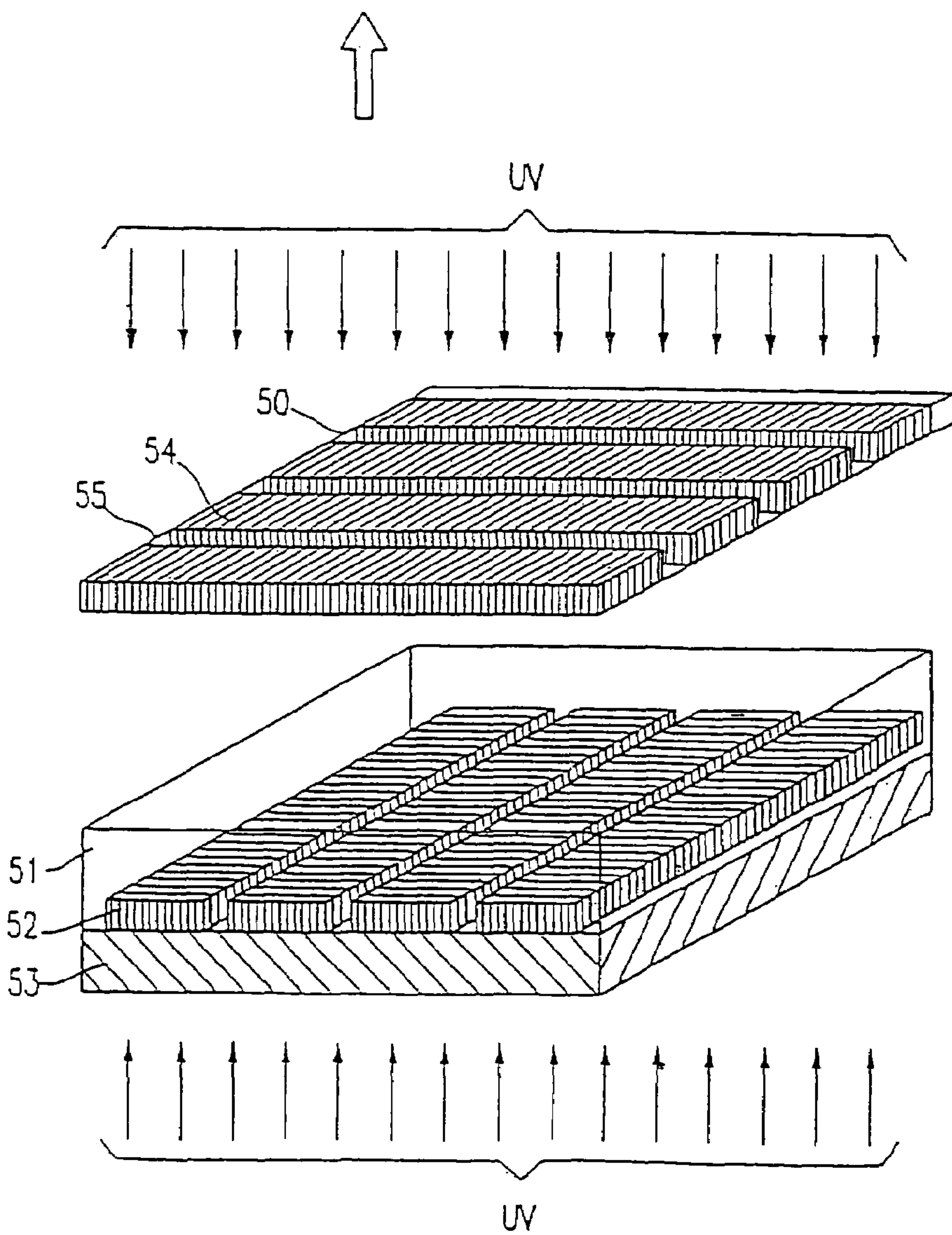
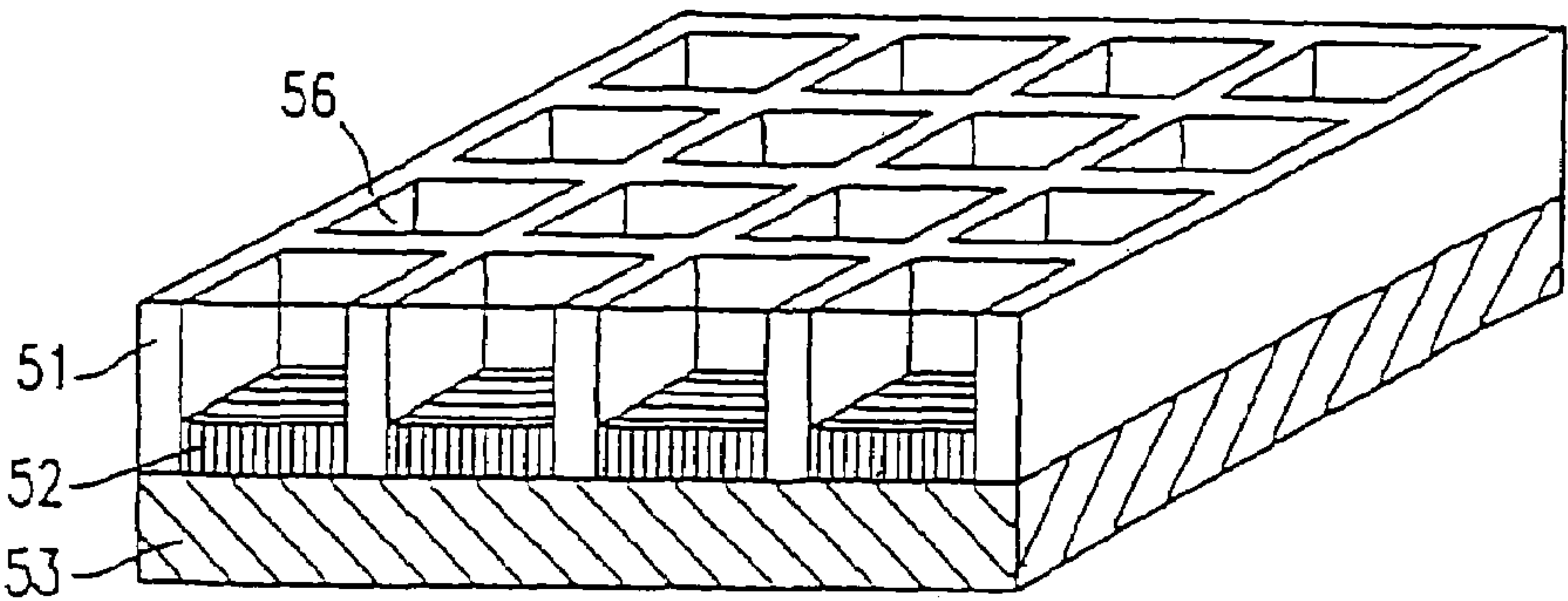


FIG. 5b1



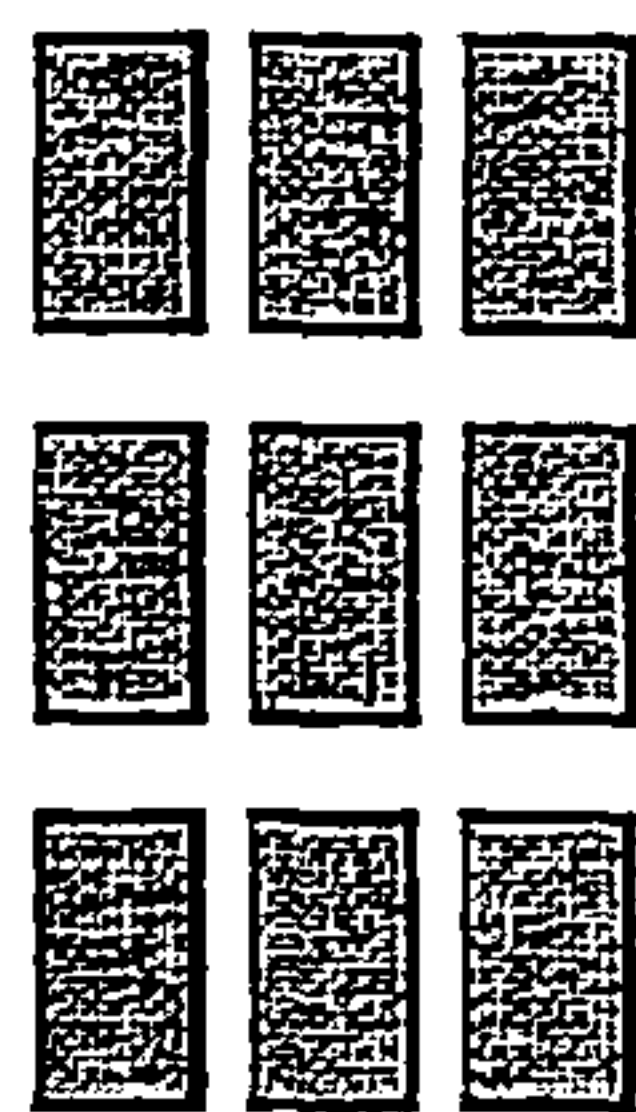


FIG. 6a

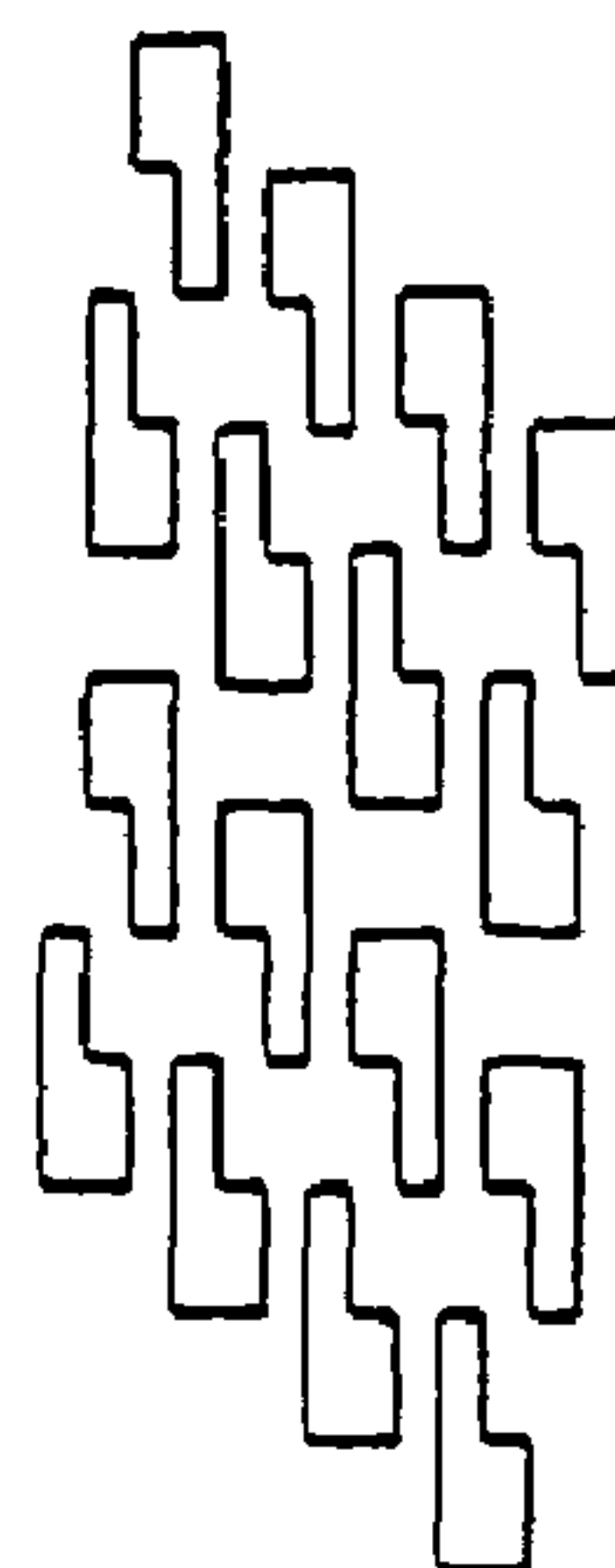


FIG. 6b

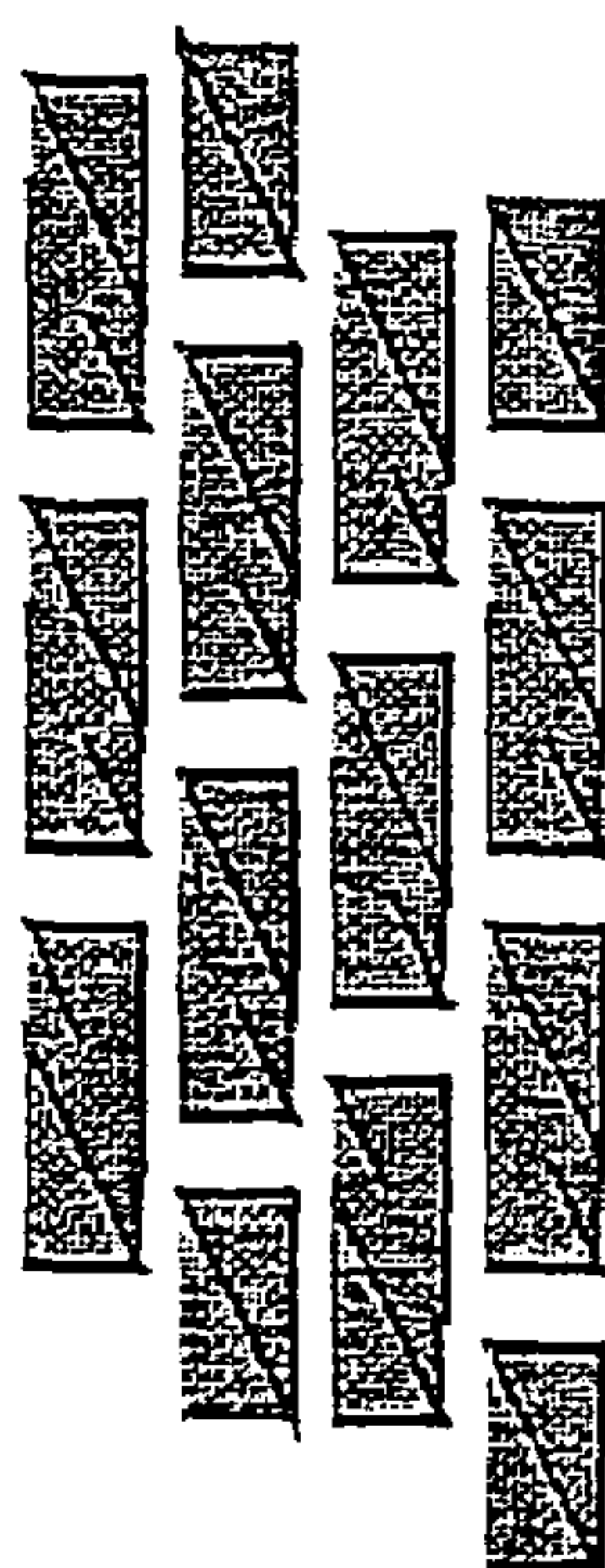


FIG. 6c

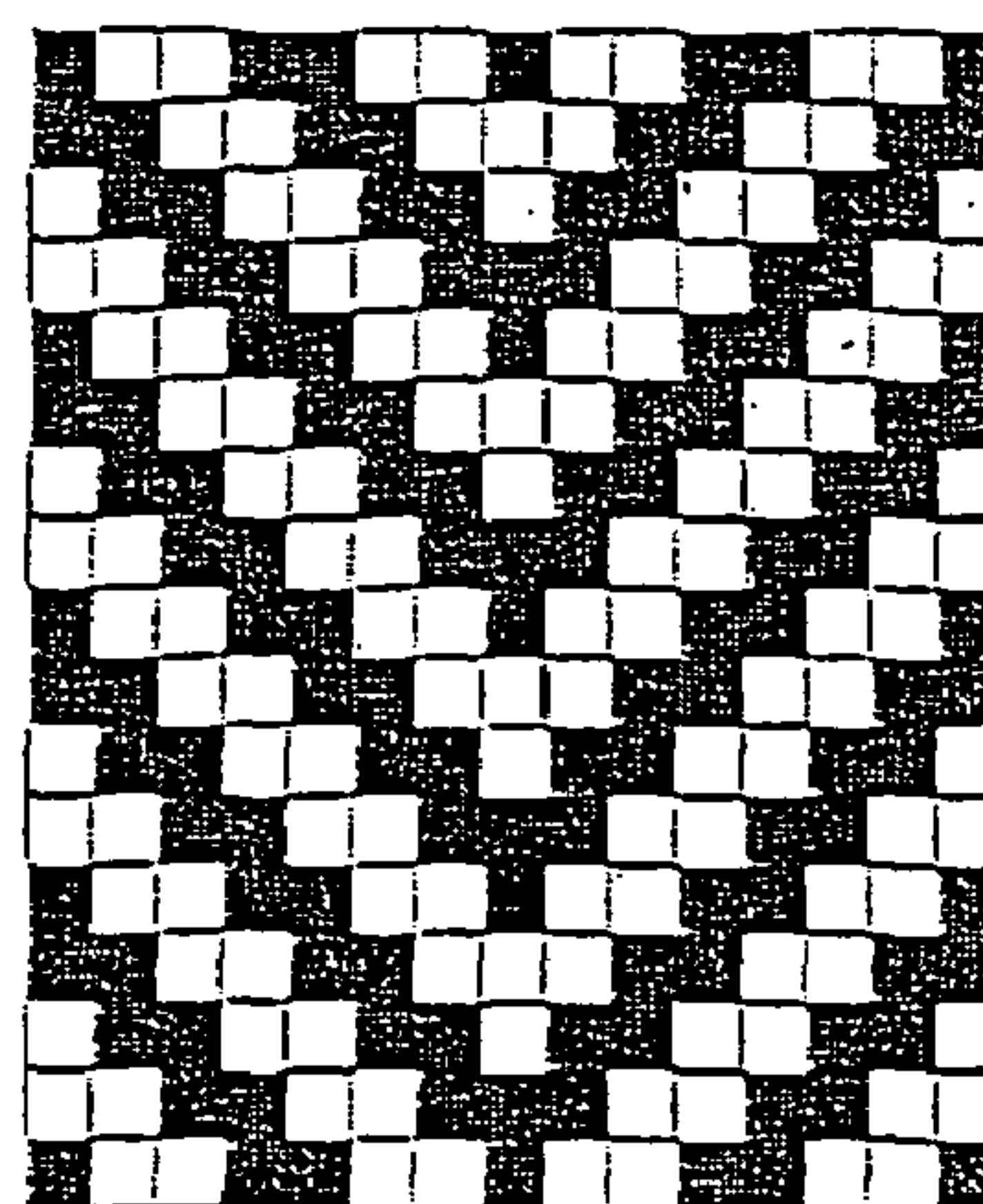


FIG. 6d

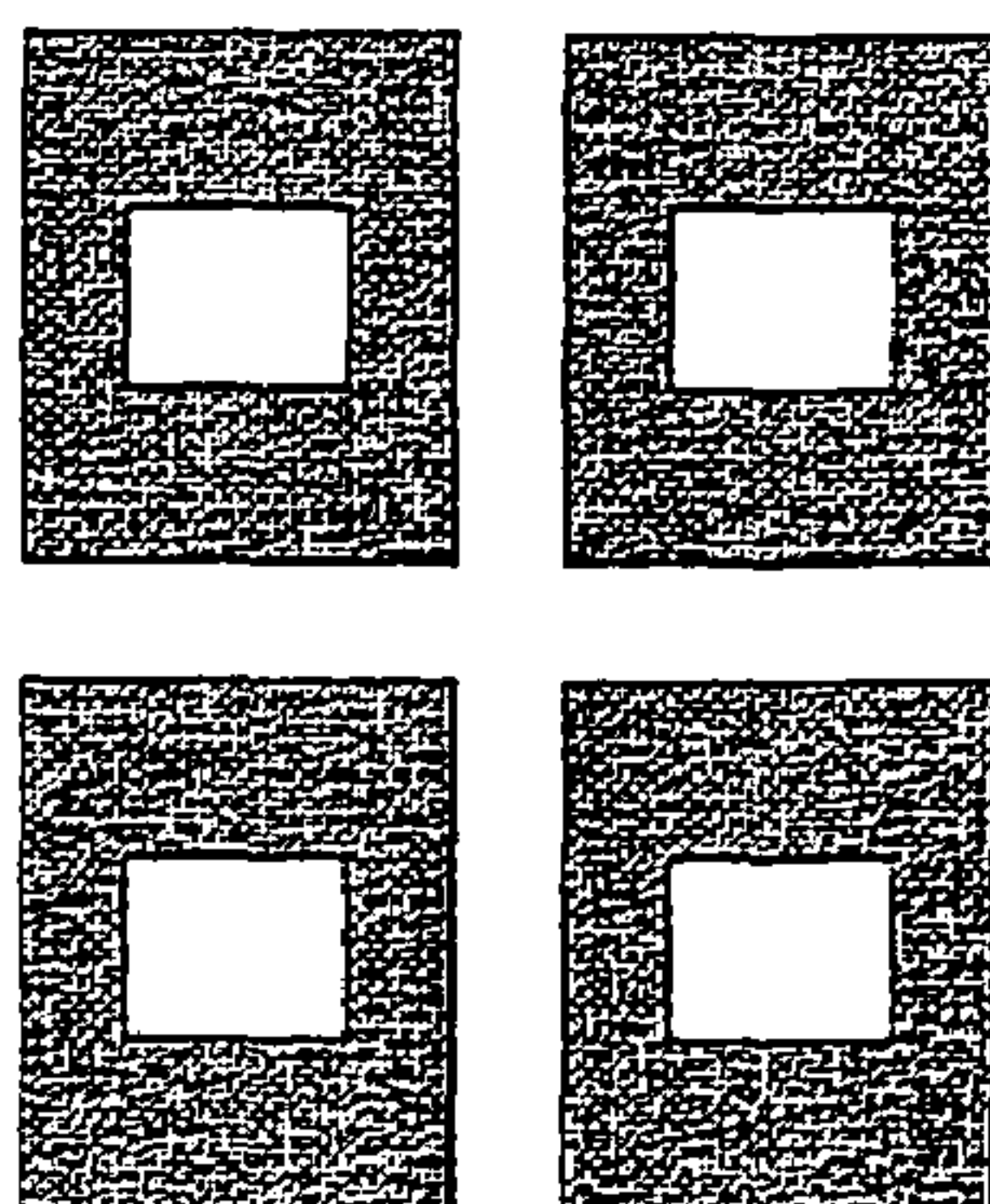


FIG. 6e

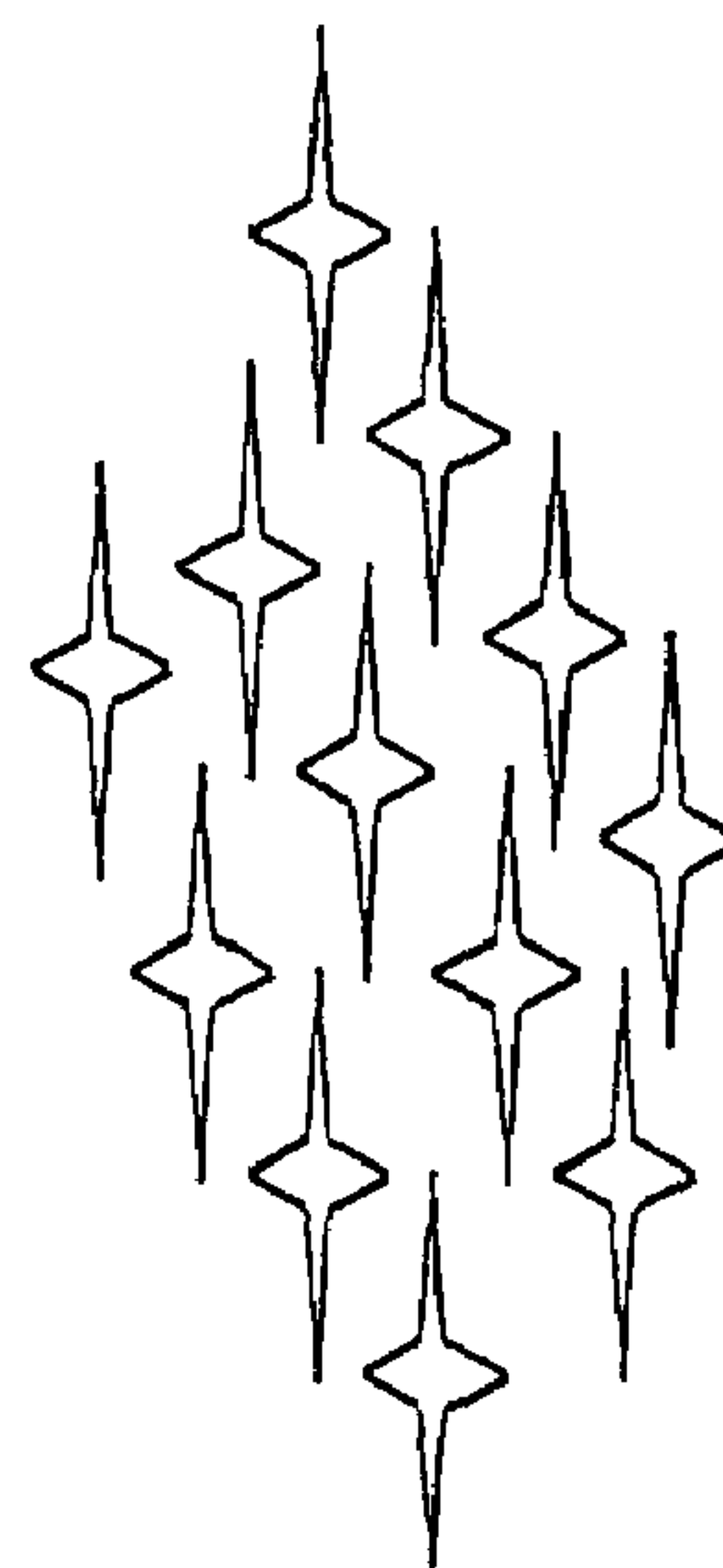


FIG. 6f

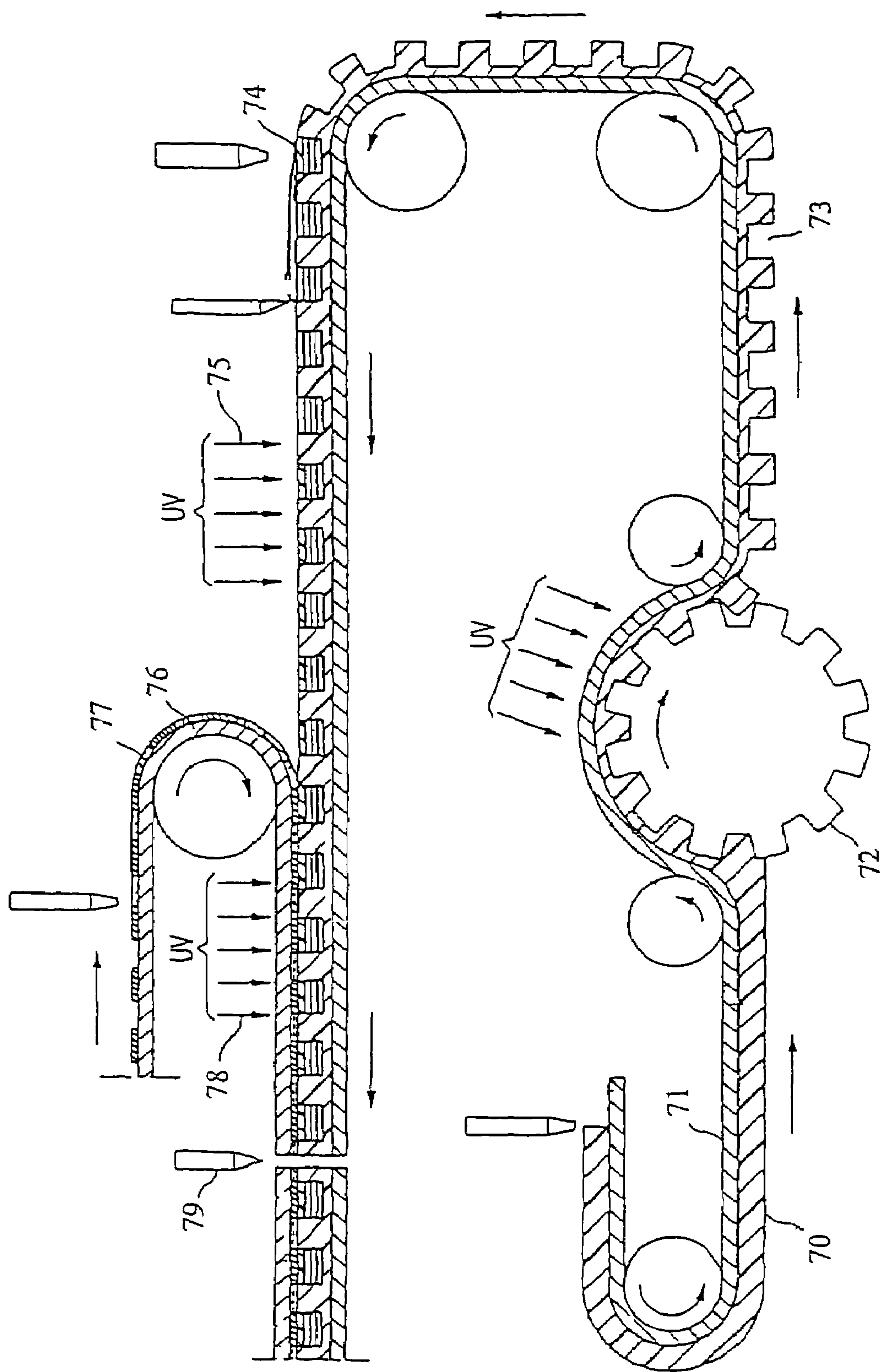


FIG. 7

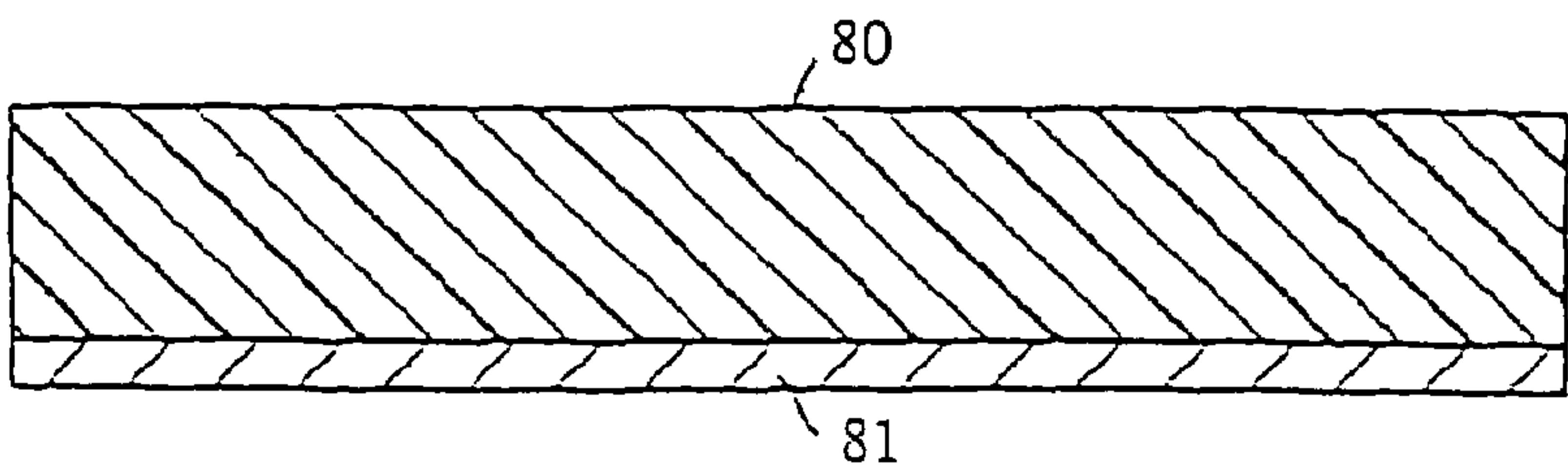


FIG. 8a

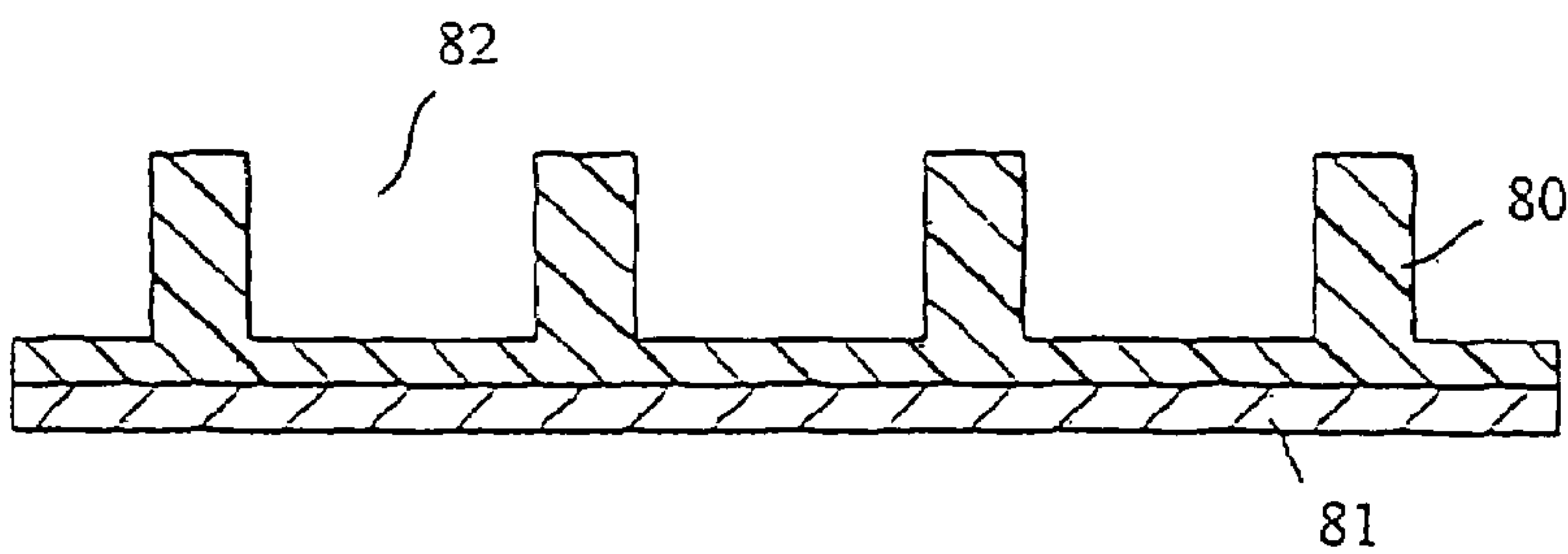


FIG. 8b

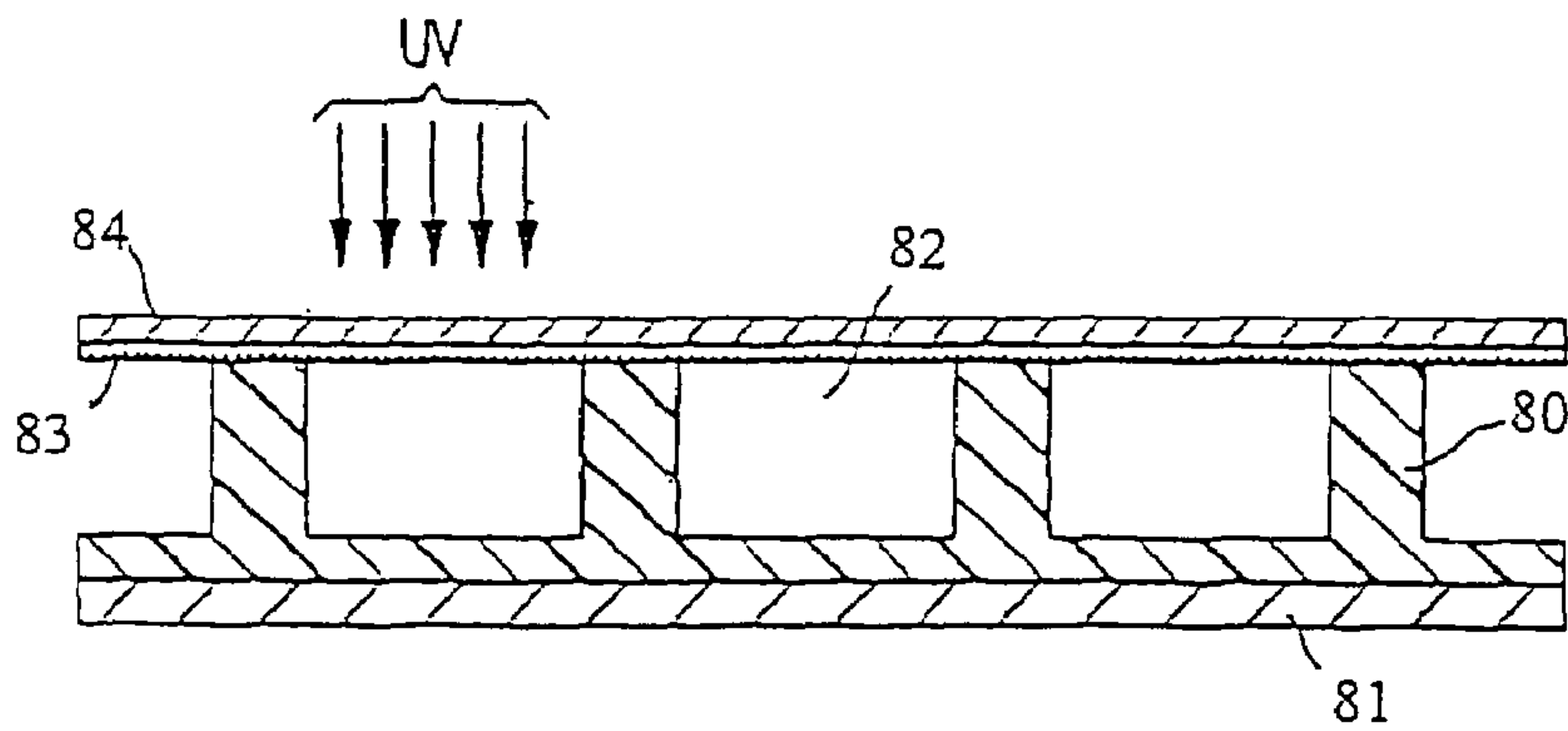


FIG. 8c

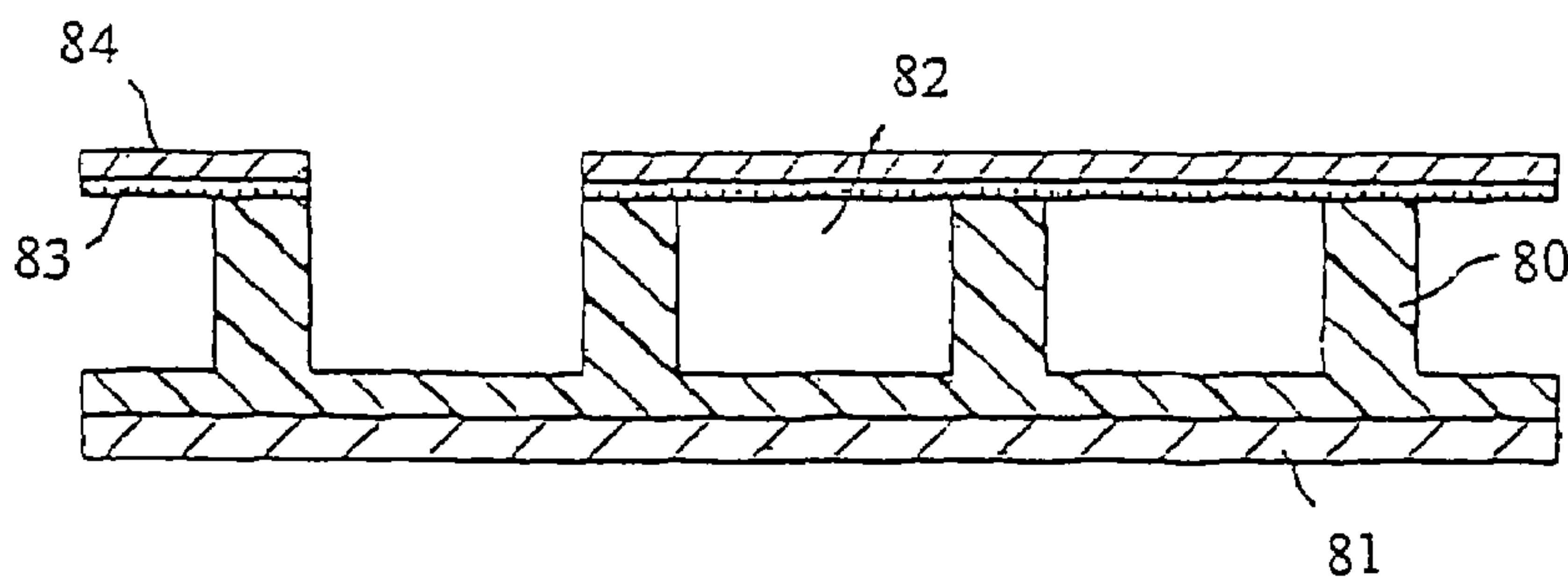
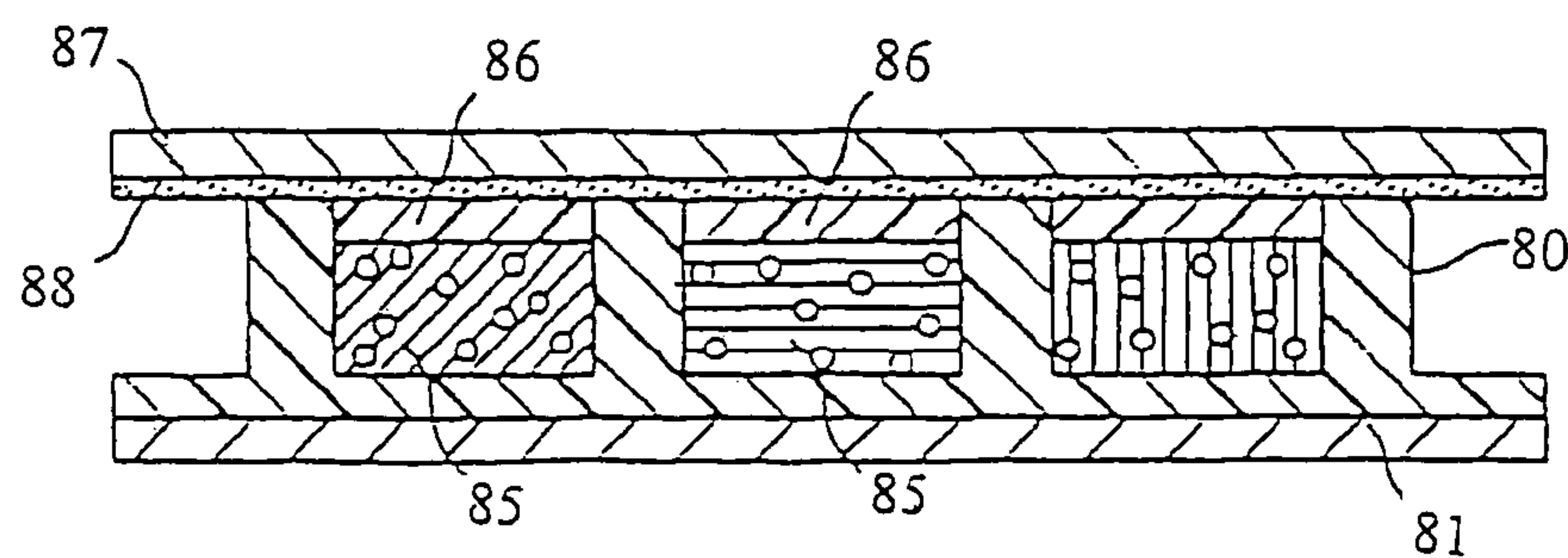
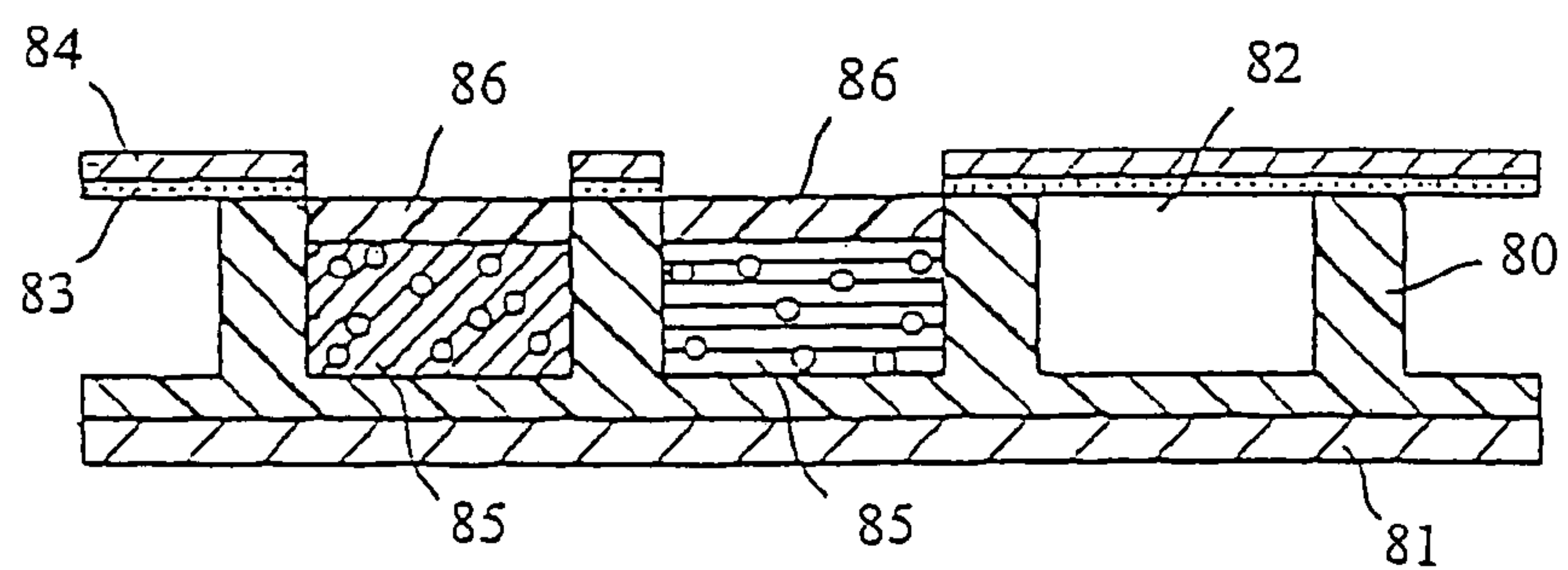
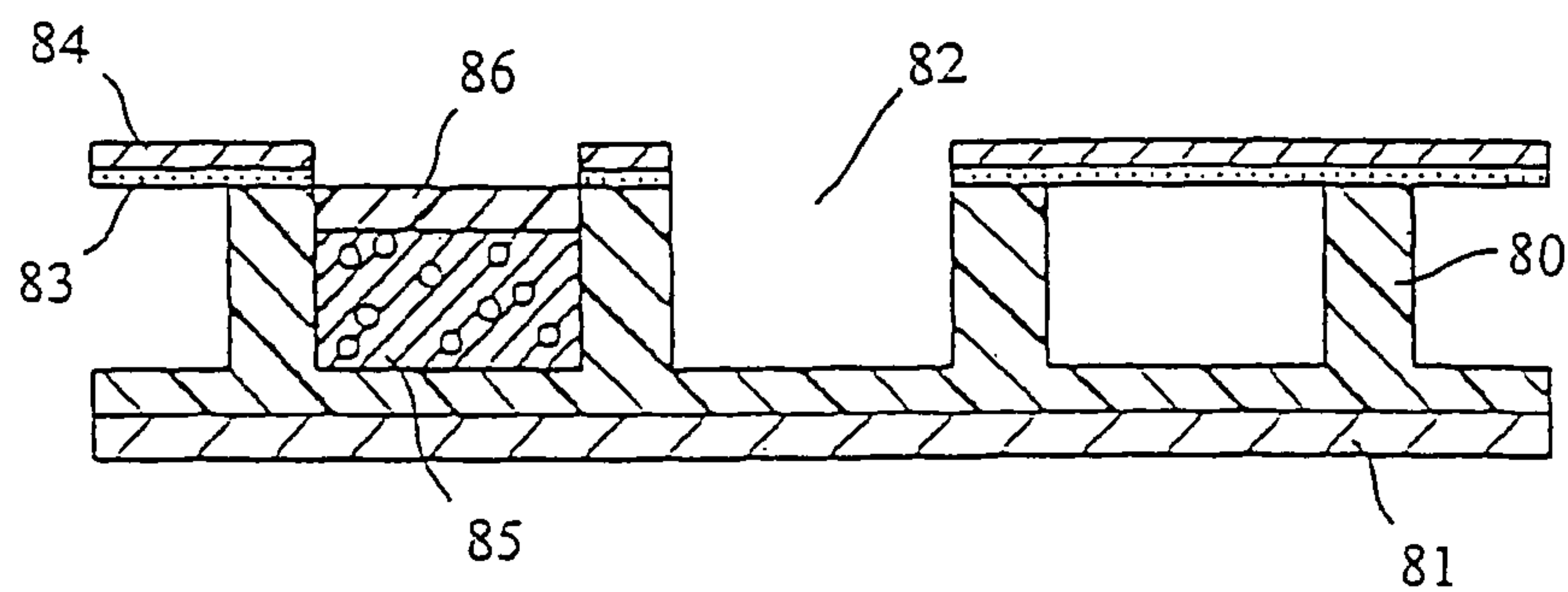
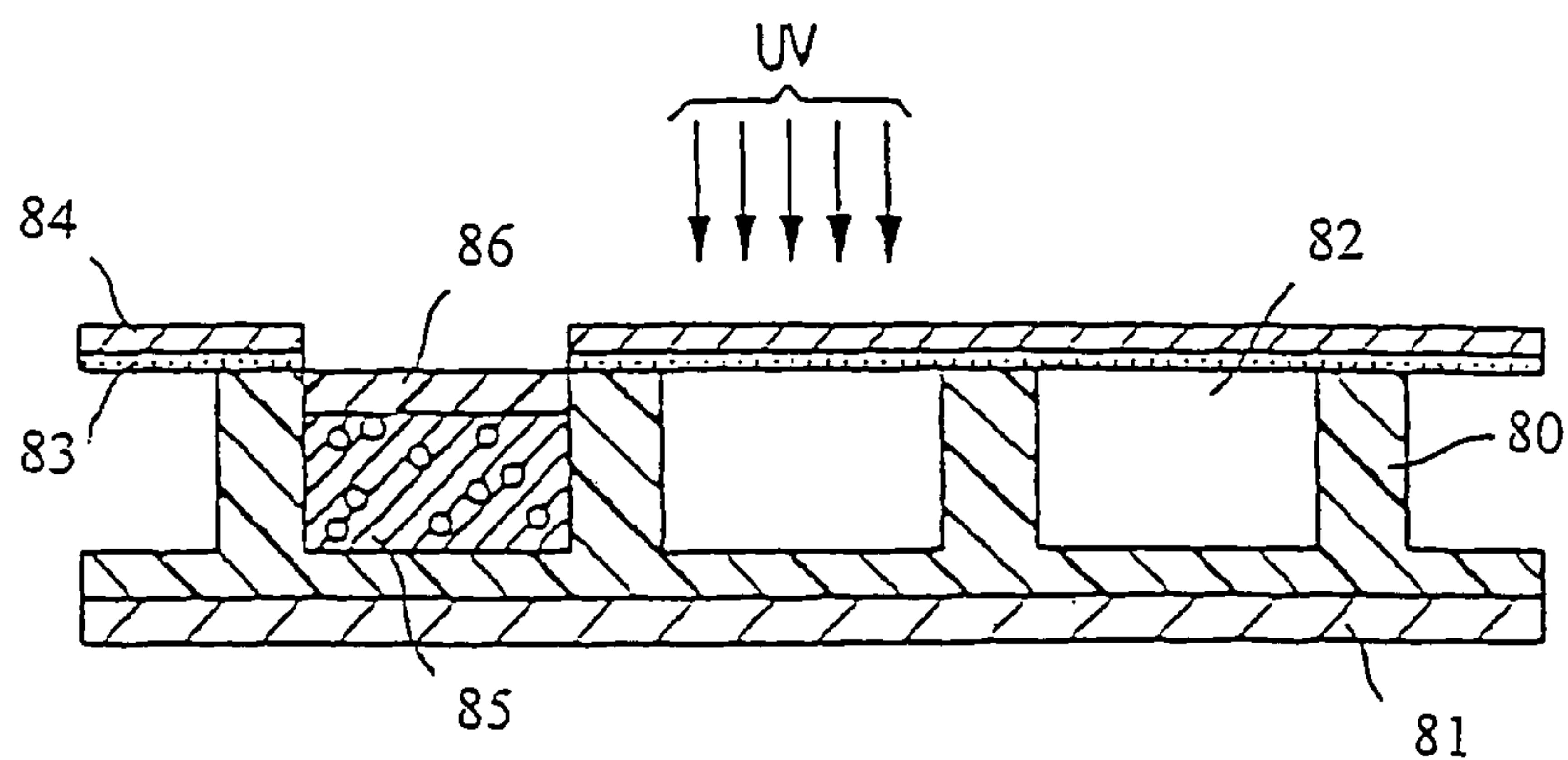


FIG. 8d



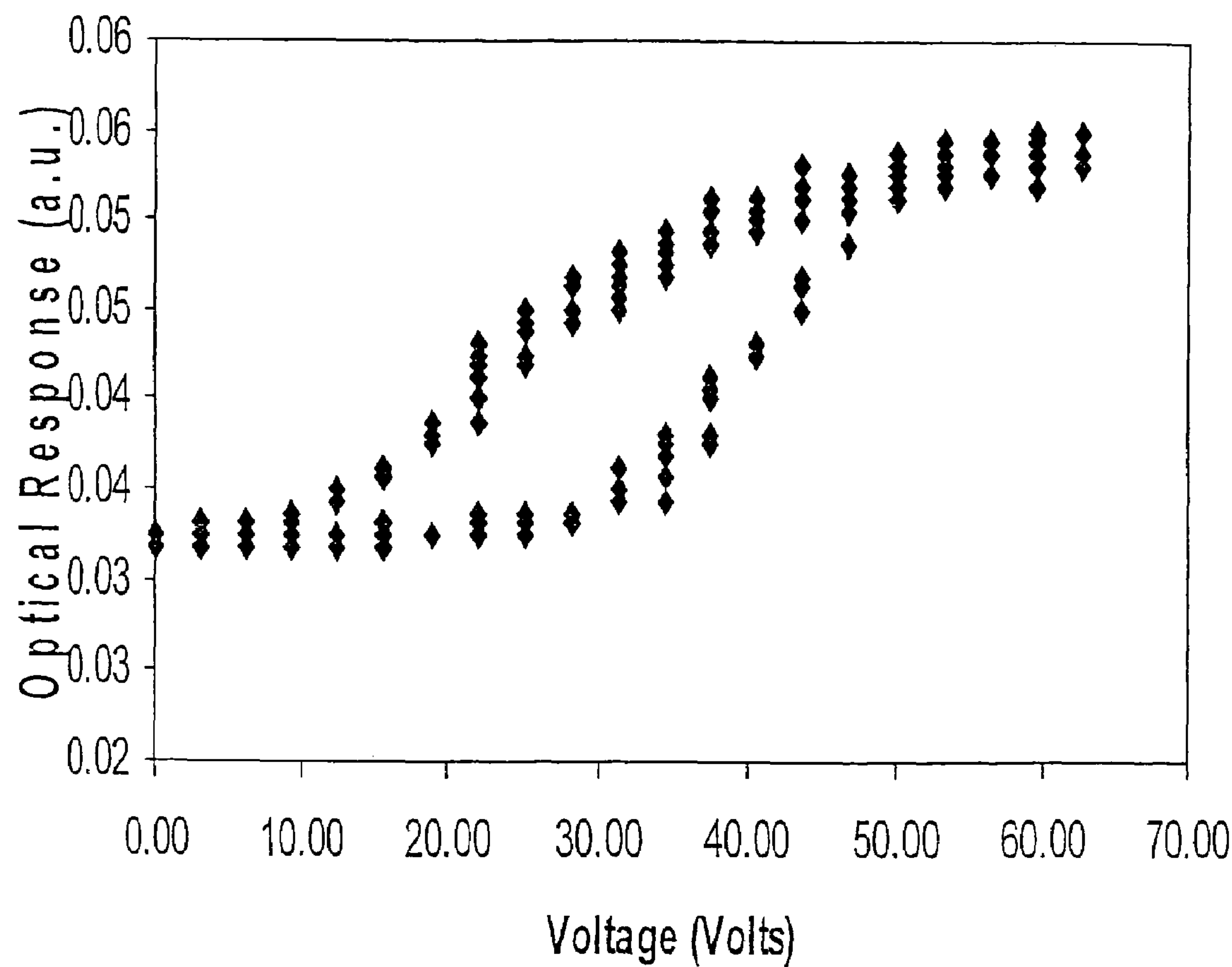


FIG. 9a
Hysteresis Curve of Conventional PDLC

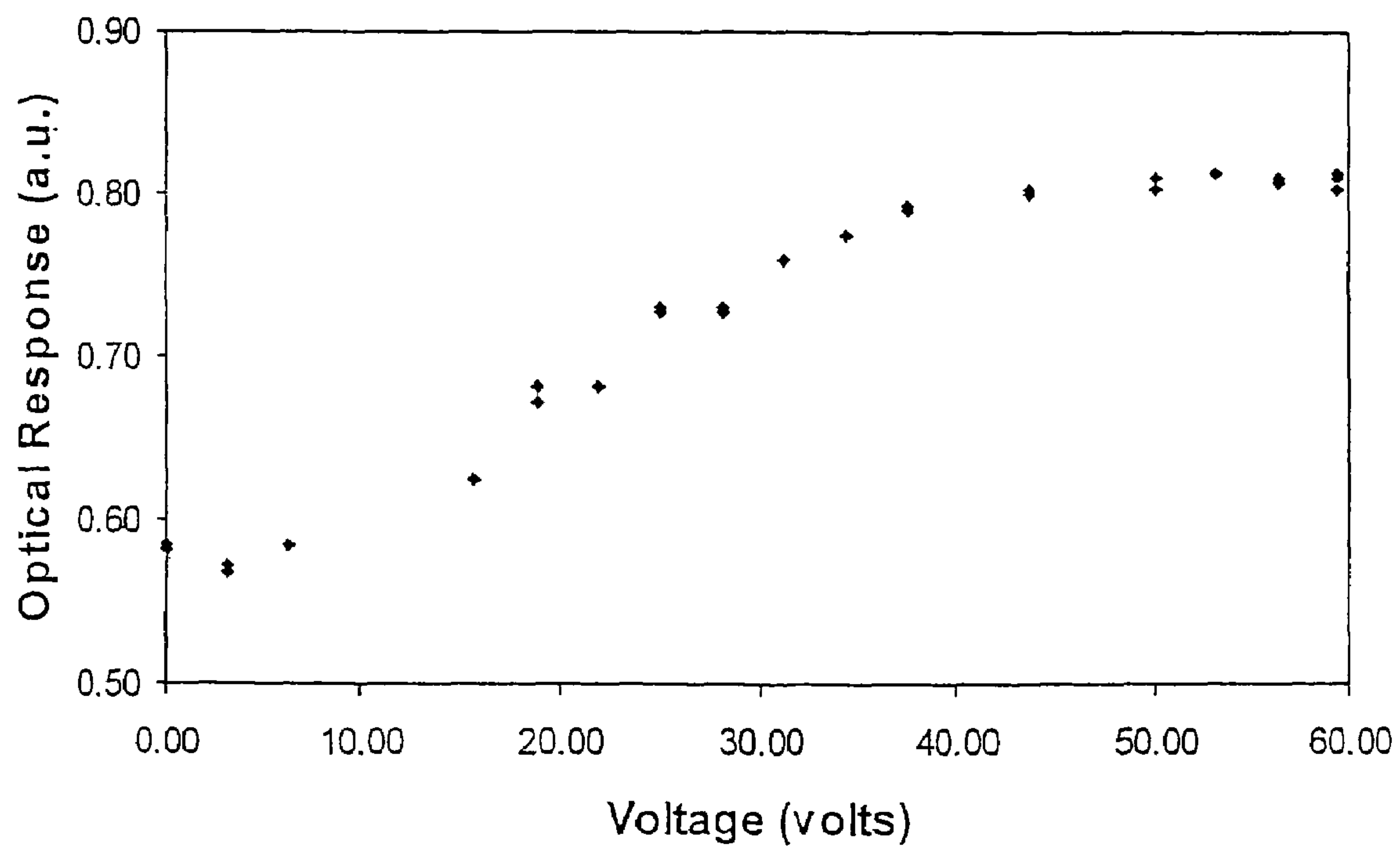


FIG. 9b

Hysteresis Curve of a LCD of the Current Invention

TRANSMISSIVE OR REFLECTIVE LIQUID CRYSTAL DISPLAY AND PROCESS FOR ITS MANUFACTURE

This application is a continuation-in-part of U.S. application Ser. No. 10/794,318, filed Mar. 5, 2004, now U.S. Pat. No. 7,095,477, which is a continuation-in-part of U.S. application Ser. No. 09/759,212, filed Jan. 11, 2001, now U.S. Pat. No. 6,795,138, both of which are incorporated herein by reference in their entirety.

FIELD OF THE INVENTION

This invention relates to liquid crystal displays comprising cells of well-defined shape, size and aspect ratio, which are filled with liquid crystals, preferably with a guest dye, and novel processes for their manufacture.

BACKGROUND OF THE INVENTION

A polymer dispersed liquid crystal (PDLC) display usually comprises two transparent plates with electrodes placed opposing each other, separated by using spacers. A thin film of PDLC is enclosed between the two plates. The PDLC film may be up to 200 micron thick, but usually having a thickness of between 2 microns and 50 microns. The cell is hermetically sealed in order to eliminate oxygen and moisture, both of which may chemically attack the liquid crystals. A thorough review of the PDLC technologies can be found in the book, "Liquid Crystal Dispersions" by P. S. Drzaic (1995). Bistable displays of this type using cholesteric liquid crystals have also been taught in, for example, S. W. Stephenson, et al, SID'04 Digest, p. 774 (2004) and D.-K. Yang, et al, SID'03 Digest, p. 959 (2003).

A PDLC typically consists of micron-size droplets of a low-molecular-weight nematic liquid crystal dispersed in a polymer binder. The nematic droplets strongly scatter light and the material has a white opaque or translucent appearance ("off state"). When a voltage difference is imposed between the two electrodes ("on state"), the electric field aligns the droplets such that the ordinary refractive index of the liquid crystal nearly matches that of the isotropic polymer matrix, substantially reducing the scattering power of the droplets, and thus allowing light to transmit through. In the "on state", the cell thus appears clear or transparent, in the "off state" it appears opaque.

In a guest-host PDLC display, a dye, particularly a pleochroic or dichroic dye, is added as a guest to the liquid crystal to produce a high color contrast display. For example, because the dye molecules have a property to orientate parallel to the liquid crystal molecules, if a dichroic dye having a bar-shaped structure is added to the liquid crystal, the direction of the dye molecules also changes if the molecular direction of the liquid crystal is changed by applying an electric field on the opposing electrodes. Because this dye is made colored or not depending on the orientation direction, it is possible to switch between a colored state ("off state") and a colorless state ("on state") by applying a voltage on the two electrodes. The use of dichroic or pleochroic dyes in guest-host PDLC displays to improve the contrast ratio is well known in the art.

A PDLC display may be transmissive and/or reflective. A transmissive PDLC display has an internal illumination source. Imposing a voltage on the two electrodes allows light to pass through the cell. A typical example of a transmissive PDLC display is a PDLC overhead projector. Reflective PDLC displays typically contain a reflective black or colored filter which becomes visible in the transparent state. Reflec-

tive PDLC displays may be found in PDA (personal digital assistant) devices. Transmissive and reflective PDLC displays are particularly attractive because polarizers are eliminated. Polarizers substantially reduce light and decrease brightness of both direct view and projection displays. The absence of polarizers also gives a better viewing angle.

The PDLC displays prepared by prior art processes have many shortcomings. For example, the polymer dispersed liquid crystals typically have droplets of very broad particle size distribution, which results in significant hysteresis, higher operation voltage, poor contrast ratio, undesirable red bleedthrough, and low level of multiplexing. However, the hysteresis of PDLC films must be low to show reproducible gray scales, and low voltage operation and high contrast ratio of the device is essential for most PDA applications. Monodispersed liquid crystal particles in the micron size range have been taught in U.S. Pat. No. 5,835,174 (Clikeman, et al.), U.S. Pat. No. 5,976,405 (Clikeman, et al.), and U.S. Pat. No. 6,037,058 (Clikeman, et al.) to reduce the hysteresis and operation voltage, and improve the level of multiplexity. The contrast ratio of PDLC device prepared from the monodispersed particles remains low for most applications. To improve the contrast ratio without trade off in the thickness of the PDLC film and operation voltage, guest dyes preferably, pleochroic dyes or dichroic dyes are needed. However, the prior art processes do not allow for the precise enclosure of a high concentration of guest dyes in the liquid crystal phase during the manufacturing process, such that only a low concentration of dyes may be encapsulated in the monodispersed polymer particles. Some guest dyes may be left outside of the particles, thereby resulting in an increase in Dmin and a lower contrast ratio.

It is highly desirable to create monodispersed liquid crystal domains, which would alleviate the requirement of high operation voltage, allow high contrast ratio and high level of multiplexing, and reduce hysteresis.

SUMMARY OF THE INVENTION

The first aspect of the present invention is directed to a liquid crystal (LC) display comprising cells of substantially uniform shape, size and aspect ratio. The cells are filled with LC preferably with guest dye(s).

Another aspect of the invention relates to a novel process for the manufacture of such a LC display.

A further aspect of the invention relates to the preparation of cells of substantially uniform shape, size and aspect ratio. The cells enclose LC preferably with guest dye(s) and are formed from microcups prepared according to the present invention. Briefly, the process for the preparation of the microcups involves embossing a thermoplastic or thermoset precursor layer coated on a conductor film with a pre-patterned male mold, followed by releasing the mold before, during or after the thermoplastic or thermoset precursor layer is hardened by radiation, cooling, solvent evaporation, or other means. Alternatively, the microcups may be formed from imagewise exposure of the conductor film coated with a radiation curable layer followed by removing the unexposed areas after the exposed areas have become hardened.

Solvent-resistant, thermomechanically stable microcups having substantially monodispersed size and shape can be prepared by either one of the aforesaid methods. The size of microcups for most display applications is in the range of submicrons to 10 microns, more preferably 0.5 microns to 5 microns. The shape may be any shape, although a shape allowing a higher total area of interface between liquid crystal

and the microcups is preferred. The microcups are then filled with LC preferably with guest dye(s), and sealed.

Yet another aspect of the present invention relates to the sealing of the microcups filled with the LC, preferably with guest dye(s). Sealing can be accomplished by a variety of ways. Preferably, it is accomplished by dispersing into the LC phase before the filling step, a sealant composition containing a thermoplastic or thermoset precursor. The sealant composition is immiscible with the LC and has a specific gravity lower than that of the LC. After filling, the thermoplastic or thermoset precursor phase separates and forms a supernatant layer at the top of the LC. The sealing of the microcups is then conveniently accomplished by hardening the precursor layer by solvent evaporation, interfacial reaction, moisture, heat, or radiation. UV radiation is the preferred method to seal the microcups, although a combination of two or more curing mechanisms as described above may be used to increase the throughput of sealing. Alternatively, the sealing can be accomplished by overcoating the LC with a sealant composition containing the thermoplastic or thermoset precursor. The solvent used in the sealant composition is critical. Preferably, it is immiscible with the LC and has a specific gravity lower than that of the LC. It is also important to control the surface tension and viscosity of the sealant composition to ensure a good coating uniformity. The sealing is then accomplished by hardening the sealant composition by solvent evaporation, interfacial reaction, moisture, heat, radiation, or a combination of curing mechanisms. These sealing processes are also unique features of the present invention.

Yet another aspect of the present invention relates to the absence of the hysteresis of the LC displays. The LC displays of the present invention consist of substantially monodispersed microcups filled with liquid crystals and preferably a guest dye. The composition of the microcups is optimized such that the isotropic refractive index of the microcups is matched to the ordinary refractive index of the LC. In a manner similar to conventional PDLC displays, the LC displays of the present invention strongly scatter light in the absence of an electric field (the "off state"). When a voltage difference is applied between the two electrodes, the electric field aligns the LC which substantially reduces scattering power and allows light to transmit through the "on state". However, unlike the PDLC displays, the LC displays of this invention reach the maximum optically clear state at a much lower voltage and, when the applied voltage is withdrawn, reverts back to the original "off state" without undesirable hysteresis. The low operation voltage, fast response time, and the absence of hysteresis of the displays of the present invention are critical for high quality display applications where low power consumption, reproducible gray scales and video rate are highly desirable.

Yet another aspect of the present invention relates to the manufacture of a LC display comprising stack of layers of microcups. The processing steps include preparation of the first layer of microcups on a conductor substrate by anyone of the methods described above, filling the microcups with a LC composition, sealing, and finally laminating the sealed microcups with a second conductor substrate precoated with an adhesive layer. The adhesives can be hot-melt, heat curable, moisture curable, or radiation curable adhesives. Of particular interest, UV curable adhesives are used in the present invention. To improve the contrast ratio, more than one layer of the microcup array may be used. The processing steps include preparation of microcups, filling with the LC composition, sealing, overcoating or laminating the sealed microcup array with a second layer of the microcup forming composition, forming the second microcup array with any of the

methods described previously, preferably by the embossing method, repeating several times the steps of filling and sealing of microcups, overcoating or laminating the sealed microcups with another layer of microcup forming composition, and finally laminating the stack of microcup layers to a second conductor substrate precoated with an adhesive layer.

Yet another aspect of the present invention relates to a process for the manufacture of a full color reflective LC display by using a conductor substrate precoated with (R, G, B) color filters and preferably a black matrix. Alternatively a full color display can be prepared by laminating the pre-formed microcups with a layer of positively working photoresist, selectively opening a certain number of the microcups by imagewise exposing the positive photoresist, followed by developing the photoresist, filling the opened microcups with a LC composition containing guest dye(s), preferably dichroic dyes of a first color, and sealing the filled microcups by a sealing process described previously. These steps may be repeated to create sealed microcups filled with LC compositions containing guest dyes of a second or a third color. A black background may be used to improve the contrast ratio and color saturation.

These multiple-step processes as disclosed may be carried out roll-to-roll continuously or semi-continuously. Consequently, they are suitable for high volume and low cost production. These processes are also efficient and inexpensive as compared to other processes for high volume production operations. The LC display prepared according to the present invention is not sensitive to environment, particularly not sensitive to humidity and temperature. The display may be very thin, flexible, durable, easy-to-handle, and format-flexible. Since the LC display prepared according to the present invention comprises cells of favorable aspect ratio and substantially monodispersed shape and size, the displays manufactured according to the present invention exhibit many desirable properties such as low power consumption, fast response time, high level of multiplexing, high contrast ratio, and reproducible gray scale presentation due to the absence of undesirable hysteresis.

Yet a further aspect of the present invention relates to a cholesteric liquid crystal display. The microcups in such a cholesteric liquid crystal display are filled with a cholesteric liquid crystal composition.

Yet still another aspect of the present invention relates to a microcup-based liquid crystal display wherein the microcups are filled with a liquid crystal composition comprising a chiral molecule.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1a and 1b show the "off" and "on" states respectively of a typical PDLC device.

FIGS. 1c, 1d and 1e are schematic depictions of the LC displays of the present invention.

FIGS. 2a-2d illustrate a typical method of preparing the male mold for microembossing.

FIGS. 3a-3b show the roll to roll process for the manufacture of a LCD, in particular, the creation of microcups by embossing a conductor film coated with a UV curable composition.

FIGS. 4a-4b show two SEM micrographs of microcup arrays prepared by microembossing.

FIGS. 5a1, 5a2, 5b1, 5b2, 5c1, and 5c2 show alternative processing steps for preparing the microcups involving imagewise exposure of the conductor film coated with a radiation curable material to UV radiation.

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FIGS. 6a-6f show examples of different shapes and patterns of microcup arrays.

FIG. 7 is a flow chart for manufacturing a monochrome LCD.

FIGS. 8a-8h show a process for the manufacturing of a full color display using three primary color guest dyes.

FIG. 9a shows a typical hysteresis curve for a traditional PDLC device.

FIG. 9b shows the absence of the hysteresis loop in a typical microcup LCD of this invention.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

Unless defined otherwise in this specification, all technical terms are used herein according to their conventional definitions as they are commonly used and understood by those of ordinary skill in the art.

The term "microcup" refers to the cup-like indentations created by microembossing or imagewise exposure.

The term "cell", in the context of the present invention, is intended to mean the single unit formed from a sealed microcup. The cells are filled with liquid crystals preferably with guest dye(s).

The term "well-defined", when describing the microcups or cells, is intended to indicate that the microcup or cell has a definite shape, size and aspect ratio which are pre-determined according to the specific parameters of the manufacturing process.

The term "monodispersed", when describing the microcups or cells, is intended to indicate that the microcup or cell has a narrow distribution of dimensions such as diameter, length, width, and height.

The term "aspect ratio" is a commonly known term in the art of PDLC displays. In this application, it refers to the depth to width or depth to length ratio of the microcups.

The sealing of display cells or microcups, in the context of the present application, is accomplished by the "top-sealing" methods as described herein in which the display cells or microcups are filled and top-sealed, as opposed to the conventional edge sealing process. In the conventional edge sealing process, two electrode layers and an edge seal adhesive are required to enclose and edge-seal the liquid crystal composition within the cells(s). In contrast, in the top-sealing process, the liquid crystals are enclosed and top-sealed before an electrode layer is disposed onto the display cell(s). Therefore, the term "sealing layer" throughout this application may be replaced with the term "top-sealing layer".

Preferred Embodiments

A typical PDLC display, as shown in FIG. 1a, comprises two electrode plates (10, 11), at least one of which is transparent (10), and a layer of liquid crystal domains dispersed in an isotropic polymer matrix.

FIG. 1a also shows the random direction of the liquid crystal molecules when no voltage (13) is imposed on the two electric plates (10, 11). The incoming light (14) is thus scattered (15) by the random orientation of the liquid crystal molecules.

FIG. 1b shows that the liquid crystal molecules are lined up in a certain direction when voltage (13) is imposed on the two electric plates. Incoming light (16) thus is transmitted through (17) because the ordinary refractive index of the liquid crystal matrix (12).

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A monochrome liquid crystal display of the present invention, schematically shown in FIG. 1c comprises well-defined cells (18) enclosed between the two electrodes (10, 11). The cells (18) are of substantially uniform shape and size and are filled with a LC composition. The electrode on the viewer's side is transparent and at least one of the two electrodes is patterned. A full range of color is obtained if three primary color filters (19), such as red (R), green (G), and blue (B), are used (FIG. 1d).

Alternatively, a full color display of the present invention may be obtained by filling the well-defined cells (1, 2 and 3) with a LC composition containing R, G, and B guest dyes, preferably dichroic dyes respectively. For example, the cells (1) are filled with LC with a red guest dye, adjacent cells (2) are filled with LC with a green guest dye, and adjacent cells (3) are filled with LC with a blue guest dye. The number of layers of the cells containing LC may be more than one (FIG. 1e).

The process for the preparation of such LC displays involves several aspects.

I. Preparation of the Microcups

(a) Preparation of the Male Mold

The male mold may be prepared by a photoresist process followed by either etching or electroplating. A representative example for the preparation of the male mold is given in FIGS. 2a-2d. With electroplating (FIG. 2a), a glass base (20) is sputtered with a thin layer (typically 3000 Å) of a seed metal (21) such as chrome inconel. It is then coated with a layer of photoresist (22) and exposed to UV. A mask (24) is placed between the UV and the layer of photoresist (22). The exposed areas of the photoresist become hardened. The unexposed areas are then removed by washing them with an appropriate solvent. The remaining hardened photoresist is dried and sputtered again with a thin layer of seed metal. A master (FIG. 2b) is then ready for electroforming. A typical material used for electroforming is nickel cobalt (23). Alternatively, the master can be made of nickel by nickel sulfamate electroforming or electrodeless nickel deposition as described in "Continuous manufacturing of thin cover sheet optical media", SPIE Proc. Vol. 1663, p. 324 (1992). The floor of the mold (FIG. 2d) is typically between 1 to 5 microns. The master can also be made using other microengineering techniques including e-beam writing, dry etching, chemical etching, laser writing or laser interference as described in "Replication techniques for micro-optics", SPIE Proc. Vol. 3099, pp. 76-82 (1997). Alternatively, the mold can be made by photomachining using plastics, ceramics or metals.

(b) Preparation of the Microcups by Embossing

This processing step is shown in FIGS. 3a and 3b. The male mold (30) may be placed either above (FIG. 3a) or below (FIG. 3b) the web (34). The transparent conductive substrate is constructed by forming a transparent conductor film (31) on a glass plate or a plastic substrate. A layer of a thermoplastic or thermoset precursor (32) is then coated on the conductor film. The thermoplastic or thermoset precursor layer is embossed at a temperature higher than the glass transition temperature of the thermoplastic or thermoset precursor layer by the male mold in the form of a roller, plate or belt.

The thermoplastic or thermoset precursor (32) for the preparation of the microcups (33) may be multifunctional acrylate or methacrylate, vinyl ether, epoxide and their oligomers, polymers and the like. Multifunctional acrylate and its oligomers are the most preferred. A combination of a multifunctional epoxide and a multifunctional acrylate is also very useful to achieve desirable physico-mechanical properties. A crosslinkable oligomer imparting flexibility, such as urethane acrylate or polyester acrylate, is usually also added

to improve the flexure resistance of the embossed microcups. The composition may contain polymer, oligomer, monomer and additives or only oligomer, monomer and additives. The glass transition temperatures (or Tg) for this class of materials usually range from about -70°C. to about 150°C. , preferably from about -20°C. to about 50°C. The microembossing process is typically carried out at a temperature higher than the Tg. A heated male mold or a heated housing substrate against which the mold presses may be used to control the microembossing temperature and pressure.

As shown in FIGS. 3a and 3b, the mold is released during or after the precursor layer is hardened to reveal an array of microcups (33). The hardening of the precursor layer may be accomplished by cooling, cross-linking by radiation, heat or moisture. If the curing of the precursor is accomplished by UV radiation, UV may radiate onto the transparent conductor film from the bottom or the top of the web (34) as shown in the two figures. Alternatively, UV lamps may be placed inside the mold. In this case, the mold must be transparent to allow the UV light to radiate through the pre-patterned male mold on to the precursor layer.

FIGS. 4a and 4b show SEM micrographs of two microcup arrays prepared by microembossing.

(c) Preparation of the Microcups by Imagewise Exposure

Alternatively, the microcups may be prepared by imagewise exposure (FIG. 5a) of a radiation curable material (51) coated on the conductor film (52) to UV or other forms of radiation through a mask (50). The conductor film (52) is on a plastic substrate (53).

For a roll-to-roll process, the photomask may be synchronized with the web and move at the same speed as the latter. In the photomask (50) in FIG. 5a, the dark squares (54) represent the opaque area and the space (55) between the dark squares represents the opening area. The UV radiates through the opening area (55) onto the radiation curable material. The exposed areas become hardened and the unexposed areas (protected by the opaque area in the mask) are then removed by an appropriate solvent or developer to form the microcups (56). The solvent or developer is selected from those commonly used for dissolving or dispersing the radiation curable materials such as methylethylketone, toluene, acetone, isopropanol or the like.

FIGS. 5b and 5c illustrate two other options for the preparation of microcups by imagewise exposure. The features in these two figures are essentially the same as shown in FIG. 5a and the corresponding parts are also numbered the same. In FIG. 5b, the conductor film (52) used is opaque and pre-patterned. In this case, it may be advantageous to imagewise expose the radiation sensitive material through the conductor pattern, which serves as the photomask. The microcups (56) can then be formed by removing the unexposed areas after UV radiation. In FIG. 5c, the conductor film (52) is also opaque and line-patterned. The radiation curable material is exposed from the bottom through the conductor line pattern (52), which serves as the first photomask. A second exposure is performed from the other side through the second photomask (50) having a line pattern perpendicular to the conductor lines. The unexposed area is then removed by a solvent or developer to reveal the microcups (56).

In general, the microcups (56) can be of any shape to maximize the light scattering effect of the liquid crystal domains. The microcups are of substantially uniform size and shape in one system. However, microcups having different shapes and sizes may be used for different colors. For example, microcups filled with LC with a red guest dye may have a different shape or size from the green microcups or the blue microcups. Furthermore, a pixel may consist of different

numbers of microcups of different colors. Also, a pixel may consist of a number of small green microcups, a number of large red microcups, and a number of small blue microcups. It is not necessary to have the same shape and number for the three colors. FIGS. 6a-6f illustrate six examples of microcup patterns that may be used in the present invention.

The openings of the microcups may be round, square, rectangular, hexagonal, or any other shape. The partition area between the openings is preferably kept small in order to achieve a high color saturation and contrast ratio while maintaining desirable mechanical properties.

For LC displays of the present invention, the dimension of each individual microcup may be in the range of about 0.04 to about $100\text{ }\mu\text{m}^2$, preferably from about $0.6\text{ }\mu\text{m}^2$ to about $36\text{ }\mu\text{m}^2$. The depth of the microcups is in the range of about 1 to about 10 microns, preferably from about 2 to about 6 microns. The opening to wall ratio is in the range of from about 0.05 to about 20, preferably from about 0.2 to about 10. The distances of the openings usually are in the range of about 0.5 to about 6 microns preferably from about 1 to about 4 microns, from edge to edge of the openings.

II. Liquid Crystals, Dichroic Dyes and Their Mixtures

The thus-formed array of microcups is filled with liquid crystals, usually by a coating process. Liquid crystals may also contain a dichroic dye to impart a monochrome color to the display and to increase the contrast.

Liquid crystal materials that may be used in the present invention are well known in the art. Examples of liquid crystal materials that may be used in the present invention include, but not limited to, E7, TL205, TL213, BL006, BL009 and BL037 from E. Merck Co. (Germany). Other liquid crystal materials are also listed in U.S. Pat. No. 5,835,174 (Clikeman, et al.).

Liquid crystals in the present invention are preferred to contain guest dye(s). Guest dyes of the present invention are dichroic and are well known in the art. U.S. Pat. No. 5,589,100 (Grasso, et al) states that arylazo or poly(aryldio) dichroic dyes may be used with liquid crystal as well as lists other dichroic dyes suitable for the present invention.

The incorporation of dyes not only adds color but also can substantially improve contrast in some display applications. To be suitable, dyes must have high order parameters and proper solubility in the host liquid crystal material. High order parameter is promoted by dyes with elongated shape having a large ratio of molecular length to width, similar to the shape of the molecules of liquid crystal host material. The LC with guest dye(s) should provide good viewing characteristics, such as high contrast, high extinction, and chemical and photochemical stability. Example of dichroic dyes having a high dichroic ratio used in the present invention include the Blue AB2, Red AR1 and Yellow AG1 from Funktionfluid Gmb (Germany) and SI-486 (yellow), SI426 (red), M483 (blue), S344 (black), S428 (black) and S7 (black) from Mitsui Toatsu.

Nonionic azo and anthraquinone dyes are also useful. Examples include, but are not limited to: Oil Red EGN, Sudan Red, Sudan Blue, Oil Blue, Macrolex Blue, Solvent Blue 35, Pylam Spirit Black and Fast Spirit Black from Pylam Products Co., Arizona, Sudan Black B from Aldrich, Thermoplastic Black X-70 from BASF, anthraquinone blue, anthraquinone yellow 114, anthraquinone red 111, 135, anthraquinone green 28 from Aldrich. In any case, the dye must be chemically stable and should have a low solubility in the microcup material. Liquid crystals or dyes should not at any time attack the microcups.

Cholesteric liquid crystals may also be used in some applications. The cholesteric phase is a liquid crystal phase exhib-

ited by chiral molecules or mixtures containing chiral components. Chiral molecules do not have reflection symmetry. A cholesteric liquid crystal is similar to a nematic liquid crystal; it has long-range orientational order but no long-range positional order. It has, however, one property that is different from the nematic liquid crystal, in that it has a helical structure. In a plane perpendicular to the helical axis, the liquid crystal directors on two neighboring planes are twisted slightly with respect to one another. Cholesteric liquid crystals exhibit two stable states at zero field: the reflecting planar texture and the non-reflecting (scattering) focal conic texture. Their optical properties, such as color and reflectivity, are important in display applications. Detailed information on cholesteric liquid crystals may be found in "Reflective Liquid Crystal Displays" by Shin-Tson Wu and Deng-Ke Yang, John Wiley & Sons Ltd., (2001); "Liquid Crystal Dispersions" by Paul Drzaic, World Scientific Publishing Co., (1995); "Polymers, Liquid Crystals, and Low Dimensional Solids" ed. by N. March and M. Tosi, Plenum Press (1984); and "Polymer Liquid Crystals" ed. by A. Ciferri, W. R. Krigbaum and R. B. Meyer, Academic Press, Inc., (1982), the contents of all of which are incorporated herein by reference in their entirety.

The cholesteric phase is a spontaneously twisted analog of the nematic phase. Most of the important cholesteric materials are simply chiral analogs of nematogens in which the chirality being introduced by having a chiral center in a terminally situated alkyl or alkoxy group. A microcup-based liquid crystal display may be achieved by filling the microcups with a liquid crystal composition comprising a chiral material.

Typical chiral nematic (cholesteric) and chiral smectic materials are mixtures of various components, consisting of both chiral and non-chiral components. Suitable nematic liquid crystals may include, but are not limited to, E7, E48, E31 and E80 from E. Merck, ZOC-1020XX (Chisso Co.) and other cyanobiphenyl liquid crystals. Suitable chiral materials useful in the present invention may include, but are not limited to, cholesteryl alkyl carbonate, cholesteryl alkenyl carbonate or a derivative thereof such as cholesteryl oleyl carbonate, CB15, ZLI-4571, ZLI-811, CE2, TM74A (all from E. Merck), CM-33 (Chisso Co.), TADDOL [5-((4R,5R)-2,2-dimethyl- α,α,α' -tetra(phenanthren-9-yl)-1,3-di-oxolane-4,5-dimethanol], (S)-(+)-(9-anthryl)-2,2,2-trifluoroethanol (Aldrich) and DASE 1835 [as disclosed in "LP-4: Late-News Poster: Chiral Dopants for LCD Applications" by F. Kuschel, C. Boeffel and M. Bauer, SID 02 Digest, P-554, the content of which is incorporated herein by reference in its entirety] and a mixture thereof. Cholesteric liquid crystal mixtures suitable for this invention may include, but are not limited to, CB 15, CE2 from VWR International Limited (formerly BDH Chemicals), BL118 (from Merck) and the liquid crystal mixture consisting of BL061, E454 and C6 (e.g., 75.6% BL061, 23.9% E454 and 0.5% C6) from E. Merck, a mixture consisting of E-31LV, 4''-(2-methylbutylphenyl)-4'-(2-methylbutyl)-4-biphenyl carboxylate and 4-cyano-4'-(2-methylbutyl)-biphenyl [e.g., 50-70% Merck E-31LV, 15-25% 4''-(2-methylbutylphenyl)-4'-(2-methylbutyl)-4-biphenyl carboxylate (chiral material) and 15-25% 4-cyano-4'-(2-methylbutyl)biphenyl (chiral material)]. A list of liquid crystal materials and mixtures thereof suitable for providing the cholesteric mesophase may be found in, for example, U.S. Pat. Nos. 3,704,056, 3,680,950, 4,097,127, 5,384,067, 5,453,863 and 6,532,052, and "Polymer Liquid Crystals" by A. Ciferri, W. R. Krigbaum and R. B. Meyer, ed., Academic Press, Inc., (1982). Preferably the cholesteric liquid crystal mixture comprises from about 20 to about 60% by weight of a chiral material.

Other additives such as silica or pigments or dyes, particularly dichroic dyes may also be added to enhance the stability of the liquid crystal texture or adjust the color.

Before the filling and sealing of the liquid crystal composition in the microcups, the surface may be precoated or pretreated with an alignment layer.

The alignment layer may be deposited on a substrate. If a conductor layer is present, the alignment layer is coated or deposited onto the conductor side on the substrate. The alignment layer may be the same as those typically used in LCD manufacturing such as a polyimide, a surfactant, a coupling agent or a photoalignment polymer or oligomer. After deposition and baking, the alignment layer may be aligned by rubbing or exposure to a polarized light. In some applications, a diamond turn may be used to create microgrooves or grating structures for the LC alignment.

In general, the photoalignment polymers or oligomers may have a photoalignment functional group on the main chain or a side chain. The precursors of the photoalignment polymers and copolymers having a photoalignable functional group on the main chain or a side chain may also be useful. The functional groups may include, but are not limited to, cinnamate, coumarin, chalcone, benzolidenenaphthalidine, benzylideneacetophenone, diphenylacetylene, stilbazole, stilbene, diphenylacetylene, diazo, spiropyran and the like.

The sealing layer formed according to Section III below may also serve as an alignment layer, the details of which are disclosed in a co-pending application, U.S. Ser. No. 10/771, 848, filed Feb. 4, 2004, the content of which is incorporated herein by reference in its entirety.

III. Sealing of the Microcups

The sealing of the microcups may be accomplished in a number of ways. A preferred approach is to disperse a UV curable sealant composition into the LC composition. The UV curable composition is immiscible with and has a specific gravity lower than that of the LC. The UV curable composition and the LC composition, are thoroughly blended in an in-line mixer and immediately coated onto the microcups with a precision coating mechanism such as Myrad bar, gravure, doctor blade, slot coating or slit coating. Volatile solvents may be used to control the viscosity, the coverage of the coating, and facilitate the phase separation of the sealant phase from the LC phase. Excess fluid may be scraped away by a wiper blade or a similar device. The thus-filled microcups are then dried and the UV curable composition floats to the top of the LC. The microcups may be sealed by curing the supernatant UV curable layer during or after it floats to the top. UV or other forms of radiation such as visible light, IR and electron beam may be used to cure and seal the microcups. Alternatively, heat or moisture, or the combination may also be employed to cure and seal the microcups, when heat or moisture curable sealant compositions are used.

Surfactants may be used to improve the adhesion of the sealant to the microcup wall and the wetting at the interface between the LC and the sealing materials. Useful surfactants include the FC surfactants from 3M Company, Zonyl fluorosurfactants from DuPont, fluoroacrylates, fluoromethacrylates, fluoro-substituted long chain alcohols, perfluoro-substituted long chain carboxylic acids and their derivatives, and Silwet surfactants from OSI.

Alternatively, the LC and the sealant composition may be coated sequentially into the microcups. Thus, the sealing of the microcups may be accomplished by overcoating a thin layer of a thermoplastic or thermoset precursor composition which is curable by radiation, heat, moisture or interfacial reactions and curing on the surface of the filled microcups. Interfacial polymerization followed by UV curing is very

beneficial to the sealing process. Intermixing between the LC layer and the overcoat can be significantly suppressed by the formation of a thin barrier layer at the interface by interfacial polymerization. The sealing is then completed by a post curing step, preferably by UV radiation. To further reduce the degree of intermixing, it is highly desirable that the specific gravity of the overcoating is lower than that of the LC. Volatile organic solvents may be used to adjust the viscosity and the thickness of the coatings. When a volatile solvent is used in the overcoat, it is preferred that it is immiscible with the LC or the dye and has a specific gravity lower than that of the LC phase. The two-step overcoating process is particularly useful when the dye used is at least partially soluble in the sealant layer. To further reduce the degree of intermixing between the sealant layer and the LC phase, the filled microcup array may be chilled before overcoating of the sealant layer.

Alternatively, sealing of the filled microcups may be achieved by transfer laminating an adhesive layer from a release substrate onto the filled microcups, preferably followed by hardening the adhesive layer by heat, radiation or by simple solvent evaporation, and finally peeling off the release substrate. Chilling of the filled microcups is also beneficial to the sealing by transfer lamination process.

The top sealing layer may be formed of a photo alignable material. In this case, the top sealing layer may be photo aligned by a polarized light, such as UV light.

IV. Preparation of Monochrome LC Displays

The process is illustrated by the flow diagram as shown in FIG. 7. All microcups are filled with LC containing the same color guest dye(s). The process can be a continuous roll-to-roll process comprising the following steps:

1. Coat a layer of thermoplastic or thermoset precursor (70) optionally with a solvent onto a transparent conductor film (71). The solvent, if present, readily evaporates.
2. Emboss the thermoplastic or thermoset precursor layer at a temperature higher than the glass transition temperature of the thermoplastic or thermoset precursor layer by a pre-patterned male mold (72).
3. Release the mold from the thermoplastic or thermoset precursor layer preferably during or after it is hardened by proper means.
4. Fill in the thus-formed array of microcups (73) with a LC composition (74) containing a thermoplastic or thermoset precursor composition, which is incompatible with the LC and has a lower specific gravity than the LC phase.
5. Seal the microcups by hardening the thermoplastic or thermoset precursor preferably by solvent evaporation, radiation such as UV (75), or by heat or moisture during or after the thermoplastic or thermoset precursor separates and forms a supernatant layer on top of the LC phase, thus forming closed LC cells containing LC and preferably guest dye(s).
6. Laminate the sealed array of LC cells with a second conductor film (76) pre-coated with an adhesive layer (77) which may be a pressure sensitive adhesive, a hot melt adhesive, a heat, moisture, or radiation curable adhesive.

The laminate adhesive may be hardened by heat or radiation such as UV (78) through the top conductor film if the latter is transparent to the radiation. The laminated product may be cut (79) to appropriate size for device assembling.

The preparation of the microcups described above can be conveniently replaced by the alternative procedure of image-wise exposing the conductor film coated with a radiation curable material followed by removing the unexposed areas by an appropriate solvent. The sealing of the microcups may alternatively be accomplished by the overcoating or transfer

lamination processes described previously, followed by hardening the sealant over the surface of the filled microcups.

To improve the contrast ratio, more than a layer of the microcup array can be used (FIG. 1c). Thus, after hardening the sealant layer on the filled microcups (the Step 5), another layer of microcup forming composition is coated onto the sealed microcup array. The Steps 2-5 can be repeated several times until an appropriate contrast ratio is achieved. The multilayer microcup stack is then laminated with a second conductor layer, and cut to appropriate size for display assembly. It is important to note that at least one of the two conductor films is prepatterned. Also at least the conductor film at the viewer's side is transparent.

V. Preparation of Multi-Color LC displays

A multi-color LC display of the present invention can be prepared by using (R, G, B) color filters and a black matrix underneath the monochrome display prepared in the previous section (FIG. 1d). Alternatively a full color display of the present invention can be prepared by filling microcups with LC containing guest dye(s) of different colors (FIG. 1e). In addition to processes described in the preparation of monochrome displays, additional steps are required for such a color display. These additional steps include (1) laminating the already formed microcups with a positively working dry-film photoresist consisting of at least a removable support such as PET-4851 from Saint-Gobain, Worcester, Mass., a novolac positive photoresist such as Microposit S1818 from Shipley, and an alkali-developable adhesive layer such as a mixture of Nacor 72-8685 from National Starch and Carboset 515 from BF Goodrich; (2) selectively opening a certain amount of the microcups by image-wise exposing the photoresist, removing the removable support film, and developing the positive photoresist with a developer such as diluted Microposit 351 developer from Shipley; (3) filling the opened microcups with the LC with guest dye(s) of a first primary color; and (4) sealing the filled microcups as described in the preparation of monochrome displays. These additional steps may be repeated to create microcups filled with LC of second and third primary colors.

More specifically, a multi-color LC display may be prepared according to the steps as shown in FIG. 8:

1. Coat a layer of a thermoplastic or thermoset precursor (80) on a conductor film (81).
2. Emboss the thermoplastic or thermoset precursor layer at a temperature higher than its glass transition temperature by a pre-patterned male mold (not shown).
3. Release the mold from the thermoplastic or thermoset precursor layer preferably during or after it is hardened by solvent evaporation, cooling, or crosslinking by radiation, heat or moisture.
4. Laminate the thus formed array of microcups (82) with a positive dry-film photoresist, which comprises at least a positive photoresist (84) and a removable plastic cover sheet (not shown). The positive dry film photoresist may comprise an adhesive layer (83) to improve the adhesion between the microcups and the photoresist.
5. Image-wise expose (FIG. 8c) the positive photoresist by UV, visible light, or other radiation, remove the cover sheet, develop and open microcups in the exposed area. The purpose of Steps 4 and 5 is to selectively open the microcups in a predetermined area (FIG. 8d).
6. Fill in the opened microcups with a LC composition containing guest dye(s) (85) of a first primary color and a sealant composition (86), which is incompatible with the LC phase and has a lower specific gravity than the LC phase.

7. Seal the microcups to form closed LC cells containing LC with guest dye(s) of the first primary color by hardening the sealant layer by solvent evaporation or curing preferably by radiation such as UV, less preferably by heat or moisture during or after the sealant separates and forms a supernatant layer on top of the liquid crystal phase (FIG. 8e).
8. Steps 5-7 described above may be repeated to generate well-defined cells containing LC with guest dye(s) of different colors in different areas (FIGS. 8e, 8f and 8g).
9. Laminate the sealed array of LC cells to a second transparent conductor film (87) pre-coated with an adhesive layer (88) which may be a pressure sensitive adhesive, a hot melt adhesive, a heat, moisture, or radiation curable adhesive.
10. Harden the adhesive.

The preparation of the microcups described in the process above can conveniently be replaced by the alternative procedure of imagewise exposing the conductor film coated with a radiation curable material followed by removing the unexposed areas by an appropriate solvent. The sealing of the microcups may be alternatively accomplished by directly coating a layer of the thermoplastic or thermoset precursor material over the surface of the liquid phase.

The thickness of the display produced by the present processes as described can be as thin as a piece of paper. The width of the display is the width of the coating web (typically 3-90 inches). The length of the display can be anywhere from inches to thousands of feet depending on the size of the roll.

EXAMPLES

The following examples are given to enable those skilled in the art to more clearly understand and to practice the present invention. They should not be considered as limiting the scope of the invention, but merely as being illustrative and representative thereof.

Example 1

Preparation of Microcups by Microembossing

The composition shown in Table 1 was coated with a Myrad bar #6 coated onto a 2 mil PET film precoated with an ITO conductor layer from Sheldahl (Northfield, Minn.). A pre-patterned (4×4×4 microns) cobalt nickel male mold and a mold release Frekote 700-NC from Henkel were used for microembossing. The coating thickness was controlled to be about 5 microns. The coated film was then embossed by the stencil using a pressure roller at 90° C. The coating was then UV-cured for about 1 minute through the Mylar film using a Cure Zone exposure unit (ADAC Technologies) equipped with a metal fluoride lamp with an intensity of 80 mW/cm² at 365 nm. The embossed film was then released from the mold to reveal well-defined (4×4×4 microns) microcups. The microembossing was carried out using the GBC Laminator at 90° C.

TABLE 1

UV-curable Acrylate Formulation for Microcups				
No.	Description	Ingredient	Supplier	Parts
1	Epoxy acrylate	Ebecryl 600	UCB Chemicals	55
2	Polyester acrylate	Ebecryl 830	UCB Chemicals	15
3	Urethane acrylate	Ebecryl 6700	UCB Chemicals	10

TABLE 1-continued

UV-curable Acrylate Formulation for Microcups				
No.	Description	Ingredient	Supplier	Parts
4	Silicon Acrylate	Ebecryl 350	UCB Chemicals	5
5	Monomer	Sartomer SR238	Sartomer	10
6	Monomer	Sartomer SR306	Sartomer	5
7	Monomer	Sartomer SR351	Sartomer	5
8	Photo-initiator	Irgacure 500	Ciba	1
9	Synergist	Methyl diethanol amine	Aldrich	0.5
10	Solvent	MEK	Aldrich	100

Example 2

Preparation of Microcups by Microembossing

The same as Example 1 except the formulation shown in Table 2 was coated and embossed with a male mold of 4×4×4 microns.

TABLE 2

UV-curable Acrylate Formulation for Microcups				
No.	Description	Ingredient	Supplier	Parts
1	Epoxy acrylate	Ebecryl 600	UCB Chemicals	50
2	Polyester acrylate	Ebecryl 830	UCB Chemicals	15
3	Urethane acrylate	Ebecryl 6700	UCB Chemicals	10
4	Silicon acrylate	Ebecryl 350	UCB Chemicals	5
5	Monomer	Poly (ethylene glycol) methacrylate	Aldrich	5
6	Monomer	Sartomer SR238	Sartomer	5
7	Monomer	Sartomer SR306	Sartomer	5
8	Monomer	Sartomer SR351	Sartomer	5
9	Photoinitiator	Irgacure 907	Ciba	0.5
10	Solvent	MEK	Aldrich	300

A Myrad bar #12 was used. The controlled thickness was 5 microns. The microembossing was carried out using a pressure roller (GBC Laminator) heated at 90° C.

Example 3

Preparation of Microcups by Microembossing

The composition shown in Table 3 was laminated using a pressure roller between a 2 ml PET film precoated with an ITO conductor layer, and a pre-patterned (4×4×4 microns) cobalt nickel mold. The PET/ITO film was treated with a corona discharge (Electro-Technic Products, Model BD-10A, Chicago, Ill.) for 5 sec. The cobalt nickel mold was pretreated with a mold release Frekote 750-NC. The coating was then UV cured for 1 min through the PET/ITO film. The embossing film was then released from the mold to reveal well-defined (4×4×4 microns) microcups with a thickness of 5.5 microns as measured by a Mituyoto thickness gauge.

TABLE 3

UV-curable Acrylate Formulation for Microcups				
No.	Description	Ingredient	Supplier	Parts
1	Epoxy acrylate	Ebecryl 600	UCB Chemicals	40
2	Polyester acrylate	Ebecryl 830	UCB Chemicals	15

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TABLE 3-continued

UV-curable Acrylate Formulation for Microcups				
No.	Description	Ingredient	Supplier	Parts
3	Urethane acrylate	Ebecryl 6700	UCB Chemicals	10
4	Silicon acrylate	Ebecryl 350	UCB Chemicals	5
5	Monomer	Poly (ethylene glycol) methacrylate	Aldrich	15
6	Monomer	Sartomer SR238	Sartomer	5
7	Monomer	Sartomer SR306	Sartomer	5
8	Monomer	Sartomer SR351	Sartomer	5
9	Photoinitiator	Irgacure 907	Ciba	0.5

Example 4

Preparation of Filled Microcups with Liquid Crystal Solution

The microcups generated in Example 3 were washed with hexanes, then with MEK, and oven dried (66° C.) for 10 min. A liquid crystal BL006 (E. Merck Co., Germany) solution containing 1 wt % Silwet L7608 (OSi Specialties) was mixed with 9 times volume of MPK, and the resulting solution was coated on microcup using Myrad bar #16. Excess solvent in the microcup was evaporated in oven (66° C.) for 10 min.

Example 5

Preparation of Filled Microcups with Liquid Crystal Solution Containing Blue Dichroic Dye

The microcups generated in Example 3 were washed with hexanes, then with MEK, and oven dried (66° C.) for 10 min. A liquid crystal BL006 (E. Merck Co., Germany) solution containing 3 wt % dichroic dye Blue AB2 (Funktionfluid GmbH, Germany) and 1 wt % Silwet L7608 (OSi Specialties) was mixed with 9 times volume of MPK, and the resulting solution was coated on microcup using Myrad bar #16. Excess solvent on the microcup was evaporated in oven (66° C.) for 10 min.

Example 6

Preparation of Filled Microcups with Liquid Crystal Solution Containing Black Dichroic Dye Mixture

The microcups generated in Example 3 were washed with hexanes, then with MEK, and oven dried (66° C.) for 10 min. A black dichroic dye mixture was prepared by mixing three dichroic dyes Blue AB2, Red AR1, and Yellow AG1 (Funktionfluid GmbH, Germany), together a liquid crystal BL006 (E. Merck Co., Germany) solution containing 2 wt % black dichroic dye mixture and 1 wt % Silwet L7608 (OSi Specialties) was mixed with 9 times volume of MPK, and the resulting solution was coated on microcup using Myrad bar #16. Excess solvent on the microcup was evaporated in oven (66° C.) for 10 min.

Example 7

Sealing the Microcups by a Two-step (Overcoating) Process

A 10% solution of Vistalon 0106 (Exxon Mobil Chemicals) in Isopar E (Exxon Chemical) was coated onto a BL006-

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filled microcup sample prepared in Example 4, 5 or 6. The coating layer was uniform and transparent. By using a #3 Myrad bar, a sealing polymer layer with the weight coverage of 0.39 mg/in² was obtained and the thickness of the sealing polymer layer was estimated to be 0.7 μ. By using a #8 Myrad bar, a sealing polymer layer with the weight coverage of 0.75 mg/in² was obtained and the thickness of the sealing polymer layer was estimated to be 1.3 μ. The density of Vistalon 0106 was about 0.9 g/cm³.

Example 8

Sealing the Microcups by a Two-step (Overcoating) Process

Following the same procedure of Example 7, the microcups were sealed by coating a 10% solution of a carboxylated acrylic copolymer, Amphomer 28-4910 (National Starch) in 2-propanol onto the BL006-filled microcups as prepared in Example 5. The coating layer was uniform and transparent. By using a #3 Myrad bar, a sealing polymer layer with the weight coverage of 0.44 mg/in² was obtained and the thickness of the sealing polymer layer was estimated to be 0.6 μ. By using a #8 Myrad bar, a sealing polymer layer with the weight coverage of 1.0 mg/in² was obtained and the thickness of the sealing polymer layer was estimated to be 1.3 μ. The density of Amphomer 28-4910 was about 1.2 g/cm³.

Example 9

Traditional Polymerization Induced Phase Separation PDLC Display

For comparison, a traditional polymerization induced phase separation polymer dispersed liquid crystal display was prepared. Different ratio of liquid crystal E7 (E. Merck, Germany) to Norland 65 (Norland) were mixed and sandwiched between two ITO coated glasses with a spacer of either 4.5 μm, 25 μm or 50 μm. Step wedge was used to optimize the UV-curing time under Cure Zone exposure unit (ADAC Technologies). FIG. 8a shows a typical hysteresis curve for polymerization induced phase separation PDLC prepared with the above procedure.

Example 10

SiPix Hysteresis-Free Liquid Crystal Display

A single layer liquid crystal display was assembled using microcup prepared in example 1, 2 or 3. Liquid crystal with or without dichroic dye(s) was filled into microcup with procedure described in example 4, 5 or 6. These LC-filled microcups were then sealed with procedure described in example 7 or 8. No hysteresis was observed for liquid crystal displays made according to the present invention. (See FIG. 8b).

Example 11

Assembling of a Multilayer Display and its Performance

Multilayer liquid crystal display was assembled to improve display performance. Single layer liquid crystal display was made as described in example 10. Same procedure was used to emboss a second layer of microcup on top of the first LC display, to fill LC with or without dye and to seal the second layer of LC display. The registration of second layer microcup

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on the first layer was set to be off from the first layer about 0 to 10 degree to maximize light scattering. Laminate two double-layer arrays to stack up a four-layer liquid crystal display. A high contrast display was obtained with rising and falling response time of ~1 msec and ~10 msec (at 40 volts) respectively. No hysteresis loop was observed.

I claim:

1. A liquid crystal display comprising a layer of display cells wherein each of said display cells comprises partition walls and a top opening wherein said top opening is sealed with a top-sealing layer which is on top of a liquid crystal composition filled in said display cell and is formed from a sealing composition having a specific gravity lower than that of the liquid crystal composition.

2. The liquid crystal display of claim 1 wherein said chiral material is a chiral liquid crystal.

3. The liquid crystal display of claim 2 wherein said chiral liquid crystal is a cholesteric liquid crystal.

4. The liquid crystal display of claim 2 wherein said chiral liquid crystal is CB15, CE2, TM74A, BL118 or cyanobiphenyl liquid crystals comprising a chiral side chain.

5. The liquid crystal display of claim 2 wherein said chiral liquid crystal is a mixture of BL061, E454 and C6.

6. The liquid crystal display of claim 2 wherein said chiral liquid crystal is a mixture of E31LV, 4''-(2-methylbutylphenyl)-4'-(2-methylbutyl)-4-biphenyl carboxylate and 4-cyano-4'-(2-methyl)butylbiphenyl.

7. The liquid crystal display of claim 1 wherein said liquid crystal composition further comprises one or more of the following:

- a) non-chiral liquid crystals;
- b) a chiral additive; or
- c) a non-chiral additive.

8. The liquid crystal display of claim 7 wherein said liquid crystal composition comprises about 20 to about 60% by weight of a chiral material.

9. The liquid crystal display of claim 7 wherein said non-chiral liquid crystals are nematic or smectic liquid crystals.

10. The liquid crystal display of claim 7 wherein said chiral additive is cholesteryl alkyl carbonate, cholesteryl alkenyl carbonate or a derivative thereof.

11. The liquid crystal display of claim 7 wherein said non-chiral additive is a filler, a pigment or a dye.

12. The liquid crystal display of claim 11 wherein said filler is silica.

13. The liquid crystal display of claim 12 wherein said silica is nano silica particles.

14. The liquid crystal display of claim 11 wherein said dye is a dichroic dye.

15. The liquid crystal display of claim 1 further comprising an alignment layer between the layer of display cells and the liquid crystal composition.

16. The liquid crystal display of claim 15 wherein the alignment layer is aligned before the display cells are filled with the liquid crystal composition.

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17. The liquid crystal display of claim 15 wherein the alignment layer is photoaligned by a polarized light after the display cells are filled and sealed.

18. The liquid crystal display of claim 1 wherein said top-sealing layer also serves as an alignment layer.

19. The liquid crystal display of claim 18 wherein the top-sealing layer is photoaligned by a polarized light.

20. The liquid crystal display of claim 1 wherein said display cells are formed from the microcup technology.

21. The liquid crystal display of claim 1 wherein said display cells are substantially uniform in size and shape.

22. The liquid crystal display of claim 1 wherein said display cells are non-spherical.

23. The liquid crystal display of claim 1 wherein said display cells have an opening area ranging from about 0.04 to about 100 μm^2 .

24. The liquid crystal display of claim 23 wherein said display cells have an opening area ranging from about 1 to about 25 μm^2 .

25. The liquid crystal display of claim 1 wherein said display cells have an opening having a circular, polygonal, hexagonal, rectangular or square shape.

26. The liquid crystal display of claim 1 wherein said display cells have a depth in the range from about 0.5 to about 10 microns.

27. The liquid crystal display of claim 26 wherein said display cells have a depth in the range from about 2 to about 6 microns.

28. The liquid crystal display of claim 1 wherein said display cells have an opening to wall ratio in the range from about 0.05 to about 20.

29. The liquid crystal display of claim 28 wherein said display cells have an opening to wall ratio in the range from about 0.2 to about 9.

30. The liquid crystal display of claim 11 wherein said dye is a subtractive or additive color system.

31. The liquid crystal display of claim 1 wherein the display is multi-color and wherein color filters are laminated or coated onto the display.

32. The liquid crystal display of claim 31 wherein said filters are red, green, and blue color filters.

33. The liquid crystal display of claim 1 wherein said liquid crystal composition is partially filled in each of said display cells.

34. The liquid crystal display of claim 33 wherein said partially filled liquid crystal composition is in contact with said sealing layer.

35. The liquid crystal display of claim 1 wherein said sealing composition comprises a thermoplastic or thermoset precursor.

36. The liquid crystal display of claim 1 wherein said sealing composition is a UV curable composition.

37. The liquid crystal display of claim 1 comprising multiple layers of display cells.

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